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E-16-658

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BEHAVIOR OF ALUMINUM IN SOLID PROPELLANT COMBUSTION

Initial manuscript prepared by E. W. Price, Georgia Institute of Technology, for the U. S. Naval Weapons Center under Purchase Order No. N-60530-75-M-0077; Purchase Requisition No. 6080-0102-75. Submitted to Naval Weapons Center on July 28, 1978.

PREFACE

Use of powdered metals as fuel ingredients in rocket propellants has led to a substantial increase in research on combustion of metals in the last 20 years. Aluminum is the only metal that has seen extensive application, and its behavior during combustion has proven to be quite complex. Because this behavior has proven to be important in many applications, it has received particularly intensive study especially in the U.S.A. and U.S.S.R. Unfortunately this study has been rather fragmented, and it is difficult to achieve effective application of results.

Over the period 1959 to 1978, research on this subject has been maintained at a rather modest level at the Naval Weapons Center, supported at various times by the Naval Ordnance Systems Command (now Naval Sea Systems Command), the Navy Strategic Systems Project Office, and the National Aeronautics and Space Agency. This work has been reported in a variety of media, indicated in the bibliography. The present report was undertaken in an effort to provide an interpretive summary of this work, particularly as it pertained to solid propellant motor applications. It is a companion to an earlier report, concerned primarily with combustion instability with aluminized propellants (NWC TP 5505).

During the rather prolonged preparation of this report, a book by Pokhil, Belyayev, Frolov, Logachev and Korotkov on the subject of "Combustion of Powdered Metals in Active Media" became available. This book summarized most of the rather extensive unclassified Russian work on the subject. With this major contribution to the subject, it was considered timely to extend the objectives of the present report, to provide an applications-oriented review of all solid propellant-related work on

aluminum combustion. Insofar as practical limitations permitted, this is what has been done. The shortcoming of incompleteness is inevitable, but hopefully not offensive. Neither the research on aluminum combustion nor this review are complete, but the efforts at synthesis of existing knowledge seem to yield better understanding and applicability of current results and point up the more critical unresolved issues.

BEHAVIOR OF ALUMINUM IN SOLID PROPELLANT COMBUSTION

INTRODUCTION

1.1 Use of Aluminum as a Propellant Ingredient

The use of powdered metals as fuel ingredients in jet propulsion systems is motivated primarily by the high heat release in metal-oxidizer reactions. The most widely used powdered metal fuel in solid rocket applications to date is aluminum, which has been used with propellants based on ingredients containing primarily H, O, C, N, Cl. These systems lead to liquid Al_2O_3 as the principal equilibrium Al - containing reaction product.

Use of powdered aluminum has a number of secondary advantages and disadvantages that enter into its choice as a propellant ingredient. Aluminum is relatively inexpensive and available; its density increases the propellant density and hence the motor propellant loading; it is nonreactive during propellant processing and storage; its reaction products are non-toxic; it tends to suppress certain classes of unstable combustion.

Disadvantages in use of aluminum center around the slow combustion of the aluminum and the condensed phase state of the reaction product. Slow burning of aluminum droplets can lead to impulse loss due to poor combustion efficiency. The condensed phase state of the products leads to losses by lowered effective molecular weight of the combustion products, and through temperature and velocity lag in the nozzle flow. The condensed phase products also cause heat transfer problems in the

nozzle and in some control systems. In the exhaust, the condensed products give sometimes unwanted visibility and identifiability to the rocket, unwanted atmospheric effects, limitations on ground-to-rocket communication, and contamination of launch and spacecraft structures.

The foregoing advantages and disadvantages differ in importance according to the application and the constraints on design and type of propellant. Because the advantages and disadvantages are all in some measure dependent on combustion of the aluminum and/or the state of the reaction products, their optimum resolution is linked to understanding and rational control of combustion. Further, the advantages and disadvantages are highly interdependent insofar as they involve aluminum combustion. Thus controlling the combustion in an optimum manner, if or when it can be done, will prove to be a juggling act involving compromises among problem areas.

An obvious and familiar example of the juggling act arises from the reduction of aluminum content in the propellant to reduce Al_2O_3 in the exhaust (to reduce exhaust plume visibility), while trying to keep motor performance up and combustion stable. Only recently has the knowledge of aluminum combustion progressed to the point of facilitating rational trade off between these competing demands on the system. Other applicational needs continually give motivation to understand aluminum behavior better, either through research or increased familiarity with current knowledge. Because the advantages and disadvantages of aluminum are so often dependent on details or completeness of combustion of the metal and form of the reaction products, there has evolved a rather considerable level of research on combustion of aluminum and other

metals. Of particular concern has been the role of the aluminum ingredient in determining stability of the combustion-flow interaction processes responsible for oscillatory combustion. In the present report, the current knowledge is selectively summarized in a way designed for easier application to propellant-propulsion problems.

1.2 Experimental Observation of Aluminum Behavior

Early observations of combustion of the aluminum ingredient in propellants consisted of the completely routine measurements of strand burning rates, and pressure and thrust during motor static firings. Other "global" observations emerged with the applicational problems, observations such as light emission by the exhaust plume. As it became more evident that understanding of combustion details was important, highly specialized tests were developed. High speed motion picture photography was adapted for viewing burning propellant samples in pressure vessels.(R-1) Rapid depressurization quench methods were used to recover propellant samples for microscopic study of burned surfaces.(R-2) Experiments providing for quench and collection of burning aluminum droplets from the combustion zone were perfected.(R-3) Experiments were developed for burning one or a few aluminum particles in controlled oxidizing atmospheres, with photography and/or quench.(R-4) Studies were made of ignition and combustion of electrically heated aluminum wires.(R-5) Experiments were developed for observing behavior of aluminum during heating to sub-ignition temperatures.(R-6) Samples of reaction products of aluminized propellants were collected and analyzed.(R-7a) Experiments were developed to study the response of

combustion to flow disturbances and measure acoustic damping by the condensed phase products.[R-7b] These and other experiments, accompanied by some advances in theory and computational methods[R-7c], have provided increasing understanding of an exceedingly complex process by which the powdered aluminum ingredient reaches the final products, primarily Al_2O_3 droplets (particles in the exhaust plume).

1.3 Practical Considerations Motivated Research

From a rather general view, the presence of aluminum in most propellants has very little effect on combustion of the propellant itself. True, the propellant reaction products become smoky, but the burning rate of the propellant is only mildly affected in most formulations, except at very low pressures or with very fine aluminum.[R-8] Aside from the intended objective of increased heat release, and the expected consequence of a smoky exhaust, the most conspicuous effect of using "aluminized" propellants is an originally unexpected one, an almost complete elimination of oscillatory combustion (combustion instability). This effect was so widespread that it became almost axiomatic (circa 1959), although the absence of an explanation for the effect was suggestive of an intricate combustion process concerning which very little was known.[R-9] Photography of the propellant combustion revealed that the detailed behavior of the aluminum combustion was indeed very intricate, and the effect on combustion stability of the propellant became a compelling stimulus for better understanding of the aluminum combustion - especially after it was found that instability was not suppressed in some motors.[R-10] Further stimulus

came from encounters with low combustion efficiency in some motors, high two-phase flow losses in some systems, and poor propellant burning characteristics in high-aluminum content propellants for air augmented rocket motors. A substantial body of research has now been conducted on aluminum combustion behavior. Although the research raises almost as many questions as it answers, a brief review of the subject is needed now to achieve use of present knowledge and to help guide future research.

1.4 Brief Summary of Aluminum Behavior

As a preface to the review in this report of the detailed behavior of aluminum in propellant combustion, it may be helpful to present a brief description of the more characteristic aspects of behavior. It is intended that this "Introduction" thereby provide also a rational basis for the approach used in organization of the subject content of the report.

From viewing combustion photography it is evident that the aluminum powder usually collects on the receding burning surface of the propellant; that numerous particles stick together; that these "accumulates"* have varying degrees of mobility (according to the propellant, pressure, lifetime on the surface); that the accumulates eventually inflame and melt down into droplets referred to here as "agglomerates".* While agglomerate formation can occur either in the surface accumulate or after the accumulate has left the surface, it is most commonly associated with separation from the burning

* These and other terms that are used in a special sense in this report are described in the list of terminology in Appendix A for easier reference.

surface. An illustration of the accumulation-agglomeration-ignition sequences is shown in Fig. 1. Extremes from this area are a) accumulates which glow brightly before completely leaving the burning surface and never seem to melt into agglomerates, b) agglomerates that form on the burning surface and burn for some time with little or no motion before departure from the surface, and c) agglomerates that form on the surface (typically on the edge of a flake of accumulate) and progressively inflame and engulf surrounding accumulated aluminum. These variants are illustrative of the detail required to know what is happening on the burning surface of solid propellants. In all or virtually all cases, the burning aluminum droplet, comprised of many original aluminum particles (as many as 10^6) experiences most of its burning history after it leaves the propellant surface. The details of this burning are not observed well in combustion photography, because the droplets are moving rapidly and because (with appreciable aluminum content) the Al_2O_3 smoke cloud obscures the field of view. However it appears that burning time for droplets is 10^{-4} to 10^{-1} sec., mostly 2×10^{-3} to 5×10^{-2} sec. During this burning time, the droplets in a rocket motor would be moving at a speed of roughly 1 to 100 meters/sec., and thus may appreciably fill the volume of the combustion chamber.

From available knowledge it appears that the ignited aluminum droplet burns by both a detached flame and surface oxidation. In the detached flame, a veil of Al_2O_3 droplets is formed (Fig. 2a), which often obscures other details. This flame is apparently responsible for formation of about 70-95% of the Al_2O_3 product, in the form of droplets mostly less than 2μm in diameter. The surface oxidation leads

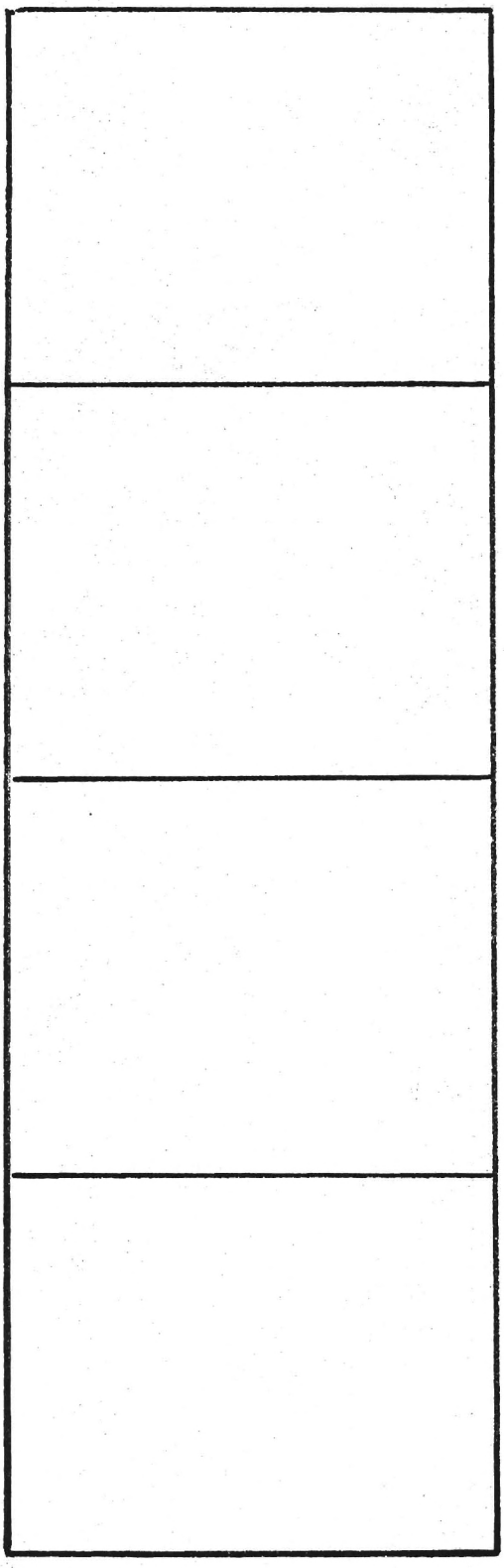
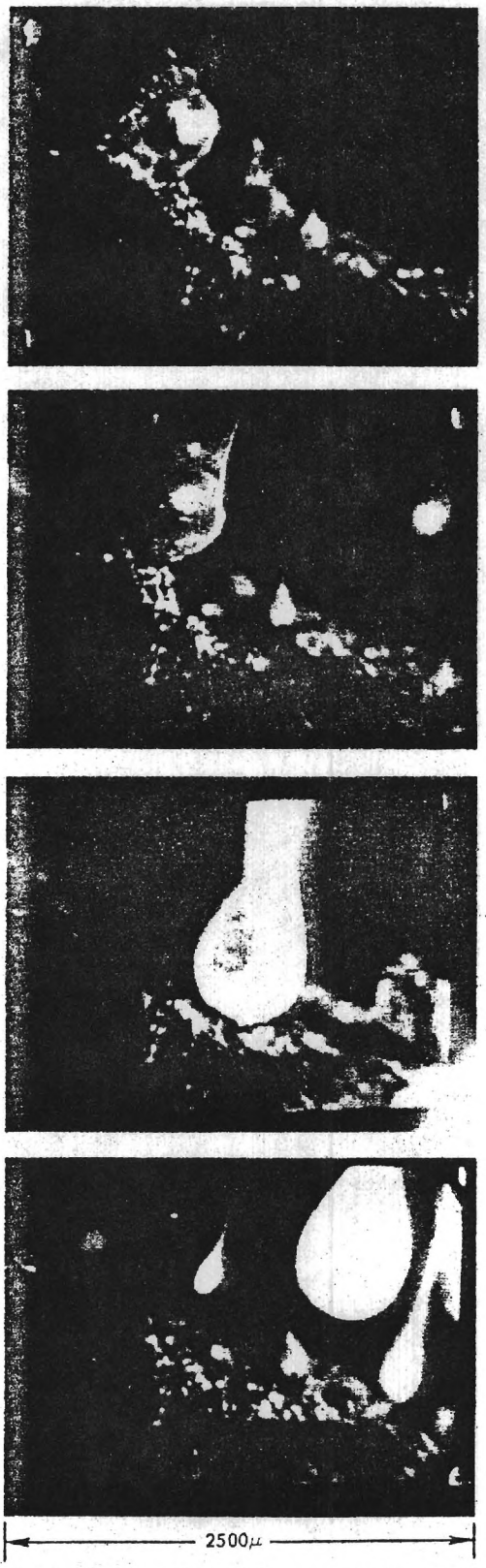
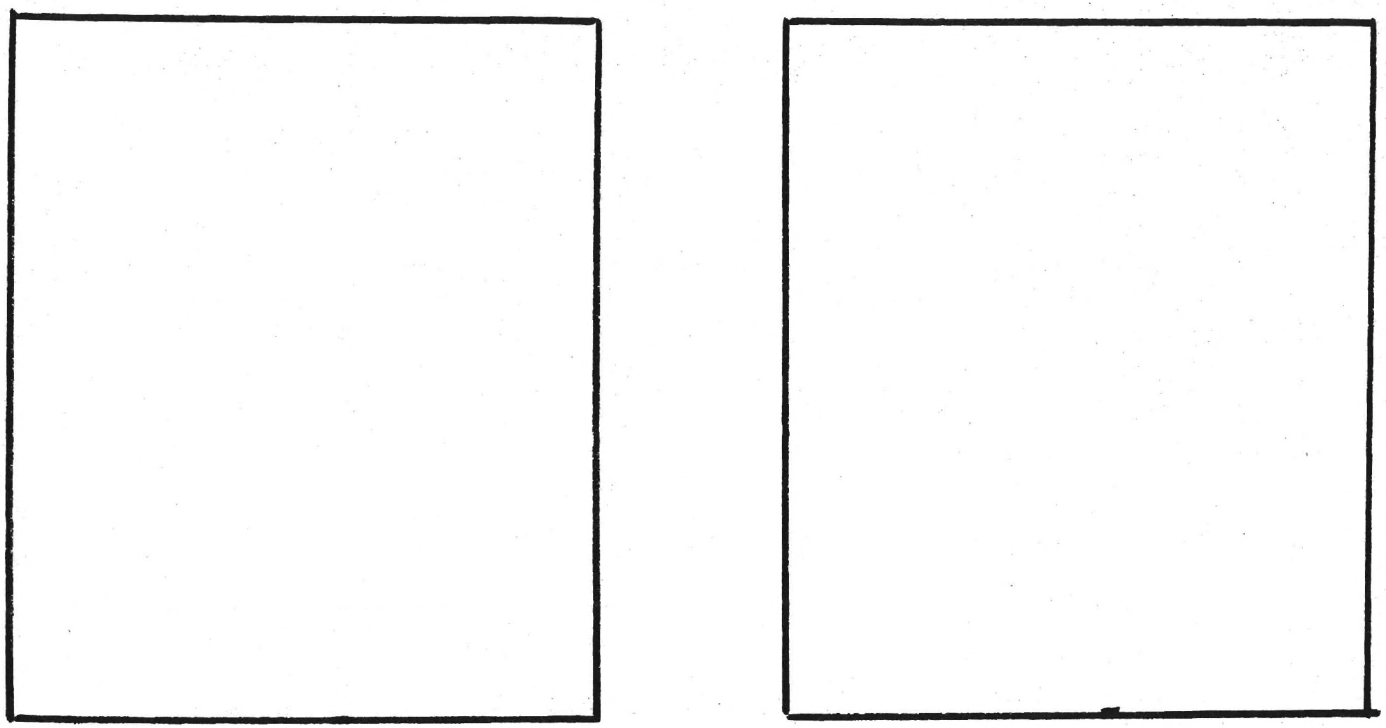


Fig. 1 Development of a burning agglomerate. Selected frames from a high speed motion picture of the burning surface of a propellant with 18% aluminum at 100 psia.



Selected frames from high speed motion picture of composite propellant containing 18% aluminum burning at 100 psi.



a b

Fig. 2. Details of a burning aluminum droplet: a) An agglomerate above a propellant burning surface, showing detached flame envelope and oxide lobe; b) Droplet and smoke cloud on a quench plate after burning in an oxygen-nitrogen atmosphere at one atmosphere, showing smoke pattern in the flame and oxide lobe on the droplet.

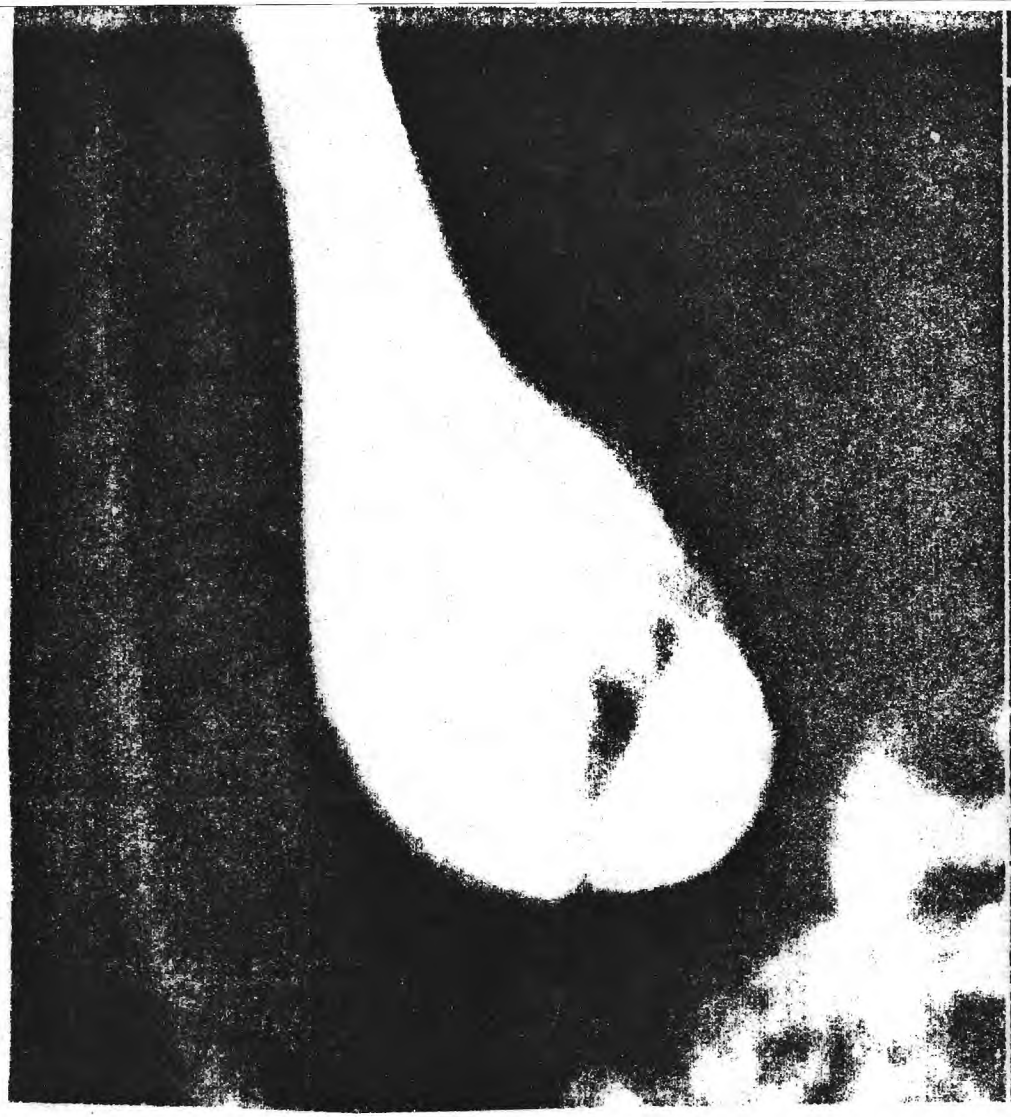


Fig. 2 a

Burning aluminum agglomerate in the Propellant Combustion Zone (from frame of 16 mm motion picture, 4000 frames per second: magnification__times)

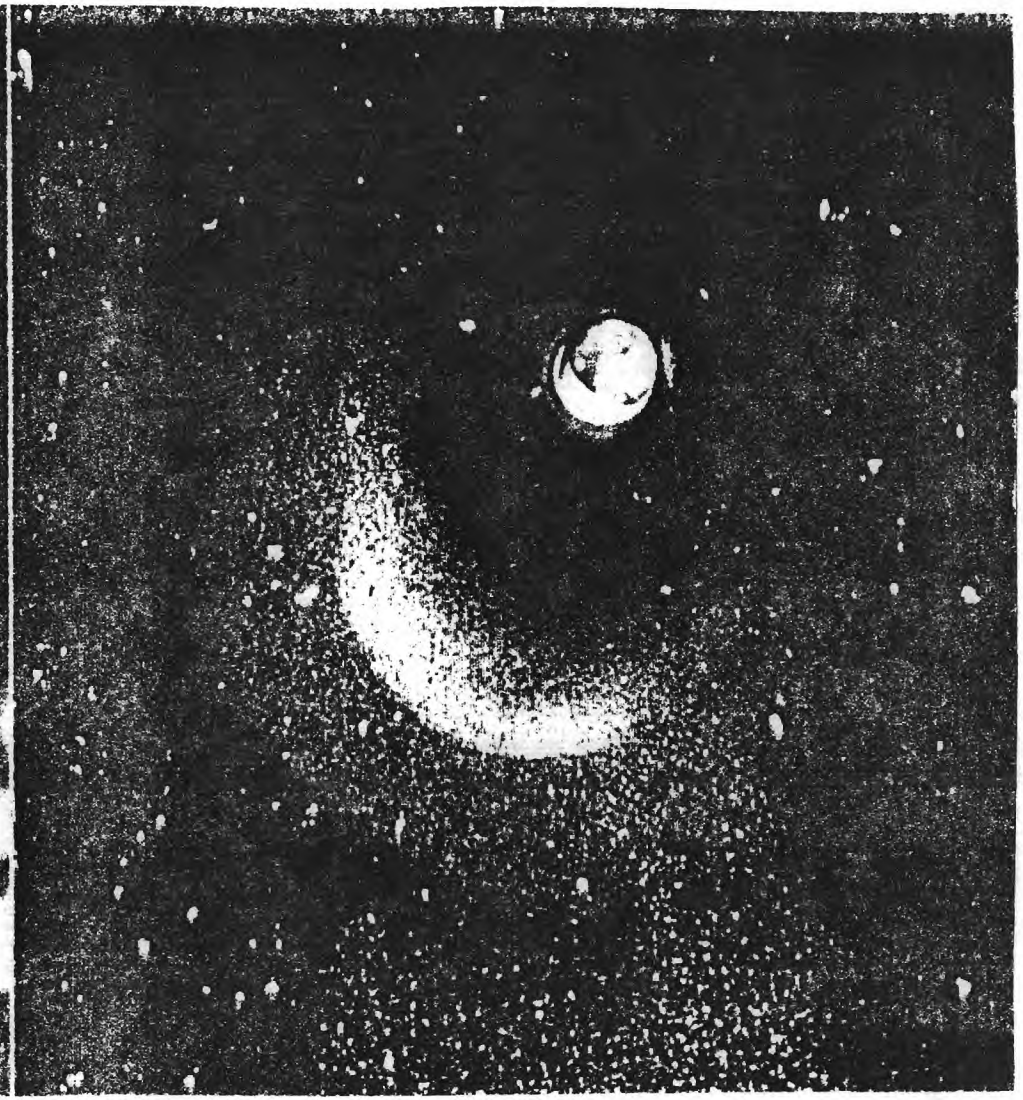


Fig. 2 b

Picture of aluminum Droplet and Associated Smoke Cloud, Quenched on a Pyrex Plate. Oxide cap on upper right ____ at one atmosphere

Fig. 2 DETAILS OF THE BURNING ALUMINUM DROPLET

to accumulation of Al_2O_3 on the droplet, Al_2O_3 that tends to migrate to form a molten lobe, (Fig. 2b), on the aluminum droplet. This accumulation leads to "residual" oxide droplets, with droplet size dependent on that of the "parent" aluminum agglomerates. This fraction of the product oxide constitutes the other 5-30% of product oxide, in the size range 2-50 μm diameter.

From the foregoing it would follow that the state of the burning aluminum droplets and oxide product would be highly spacewise non-uniform in a rocket motor. Little or no direct data on this subject is available. Some of the factors of importance include: effect of gas flow on droplet combustion and on product droplet growth, coalescence, or shattering of droplets; and effect of gas flow on the propellant surface processes such as accumulation-agglomeration-ignition.

Thus in summary, the aluminum tends to accumulate and coalesce on the propellant burning surface, eventually draws up into droplets 10 to 10^6 times larger (by mass) than the original aluminum particles. The droplets burn primarily after leaving the burning surface, with burning times of 2 to 50 milliseconds. The reaction product of the aluminum is Al_2O_3, which occurs in a "bimodal" droplet size distribution (Fig. 3) resulting from concurrent surface and detached flame oxidation of the aluminum droplets. There is considerable (sometimes unconnected) information about the steps in the combustion process, but very little about the effect of gas flow on the process.

1.5 Organization of Report

In contemplating a review of a complicated process like aluminum

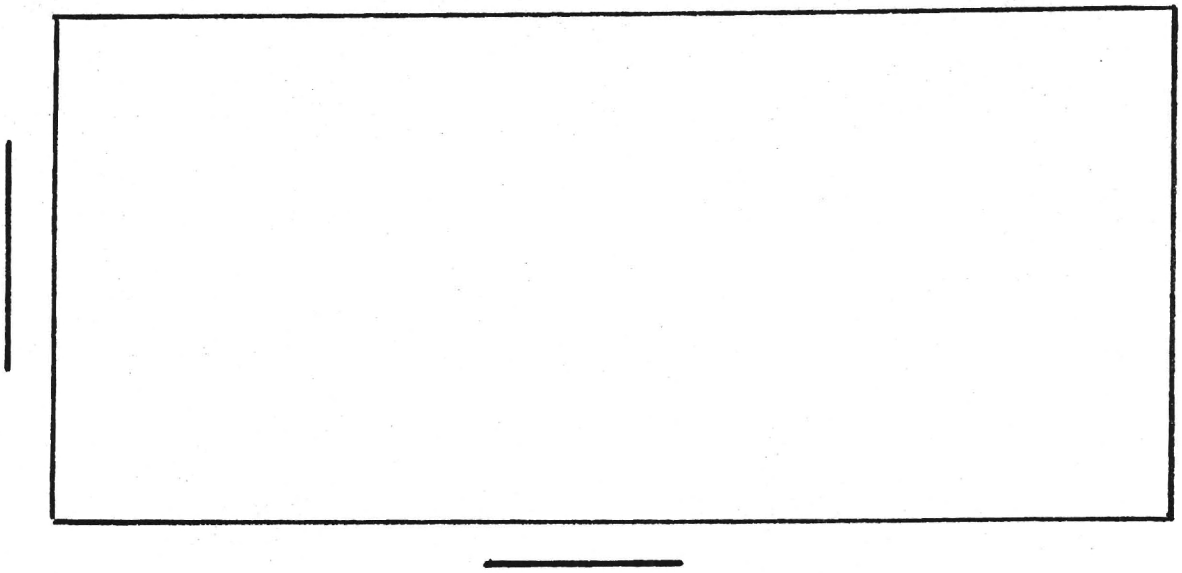


Fig. 3. Weight - diameter distribution of ingredient aluminum (H-30) and product oxide for A-199 and A-200 propellant.

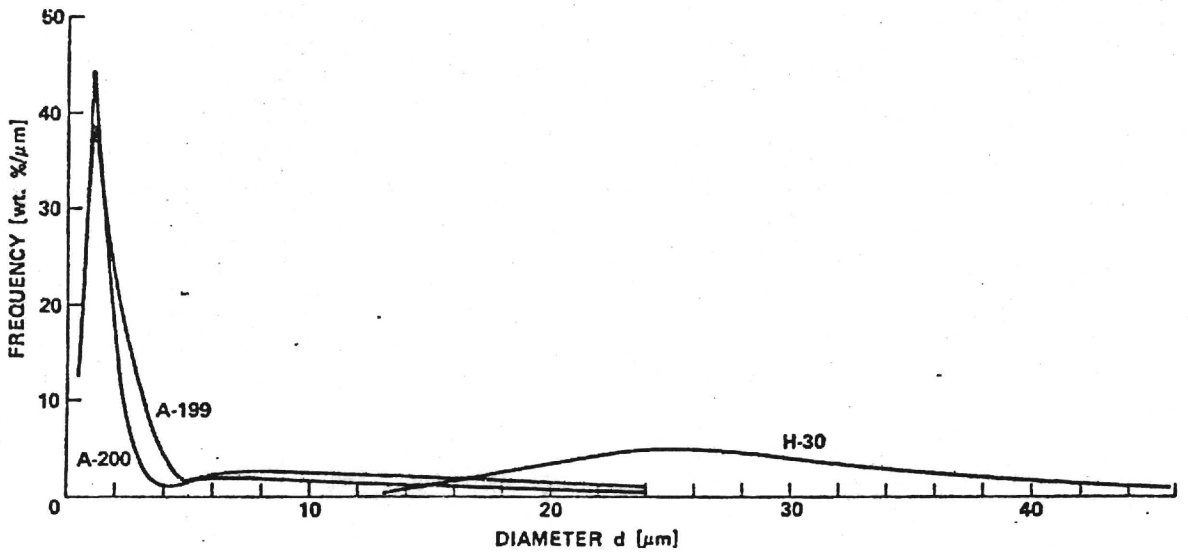


Fig. 3 Size Frequency of Residues of Propellants A-199 and A-200 and of H-30 Aluminum Powder

behavior in propellant combustion, one is confronted with a choice of rationale for organization of the subject matter, an effective choice that brings in all details naturally and ends up with a good perspective of the phenomenon. Such a choice of organization is suggested by the phenomenon itself, and has been present in the description in the preceding paragraphs. Thus the aluminum goes through a sequence of environments and responses in "passing through" the propellant combustion zone, from surface retention to accumulation and adhesion, to agglomeration and ignition, to combustion in the motor cavity with formation of Al_2O_3 products. Because these are reasonably well-defined, natural, and important steps in the aluminum behavior, they were chosen as the primary basis for organization of the review reported in the following.

THE INGREDIENT ALUMINUM

2.1 Uniqueness of Aluminum as a Propellant Ingredient

As a propellant ingredient, aluminum is unique when compared with the other ingredients. It is an element, and hence does not decompose. It has low vapor pressure, and hence does not give off reactive vapors until it is quite hot (boiling point 2493°C at 1 atm.). It melts, but only at a temperature (660°C) close to or higher than normally present on propellant burning surfaces. Its oxide (Al_2O_3) has a very high melting point (2042°C), and tends to protect the aluminum particles from chemical attack, by forming a rather impervious surface layer on the otherwise reactive particles. All of these features tend to inhibit participation of aluminum particles in the propellant combustion until they are heated appreciably by the high temperature region of the propellant flame above the propellant surface, a circumstance that has a heavy impact on the aluminum behavior.

Other properties of aluminum that are of interest in combustion are:

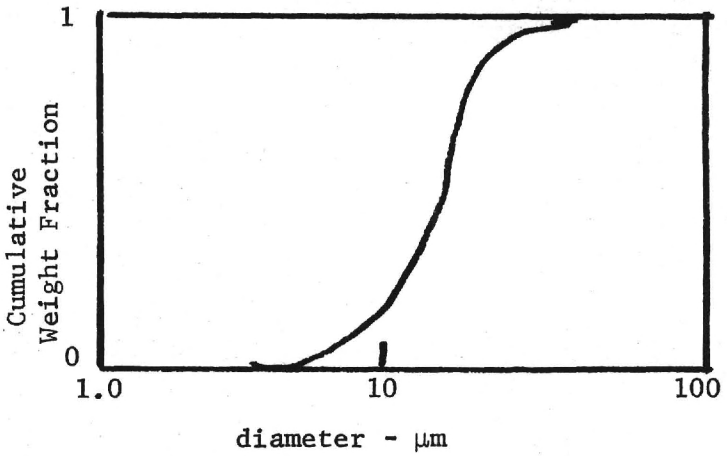
atomic weight	26.98
density, gm/cm^3 (at 20°C)	2.7
specific heat capacity, cal/gm.°C (at 20°C)	0.214
thermal conductivity, cal/cm.^{2o}C (at 20°C)	0.503
thermal expansion coefficient, linear, 10^{-6o}C (avg. 20-100°C)	23.8
latent heat of fusion, cal/gm	96.
latent heat of evaporation, cal/gm	3050.

(Values from (R-11a))

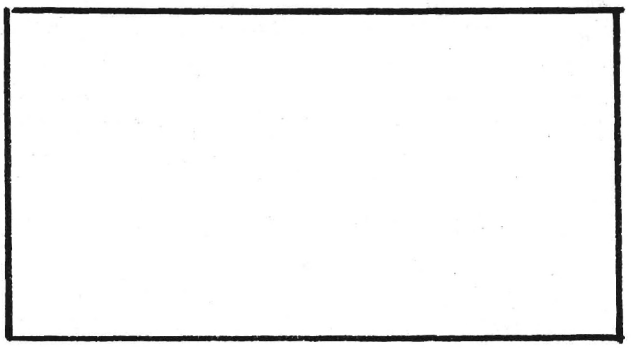
2.2 Typical Characteristics of Commercial Aluminum Powder

The characteristics of the aluminum used in propellants are dictated by practical considerations. Aluminum can be prepared in a range of particle sizes and shapes, but the choice of material used in propellants is usually dictated by cost, availability and compatibility with propellant processing as much as by any combustion considerations. Virtually all the aluminum used is atomized aluminum, produced primarily for the paint and die-casting industries. The atomization is accomplished by the aspirator action of an air stream, which draws molten aluminum ($\sim 785^{\circ}C$) from a reservoir. The (swirling) air flow atomizes the aluminum, which then flows through a cooling tank where the aluminum solidifies. Sizing is accomplished by cyclone separators and/or sieving. The particles are blobs of simple (but not really spherical) shape. A size distribution (Fig. 4a) averaging about 15 μm is probably most favored because it "packs" readily in a matrix involving typically coarser oxidizer particles. However, distributions with mass-average sizes anywhere in the range 5-50 μm are chosen in various instances, with occasional selections of finer or coarser material (1-100 μm). Figure 4b shows the shape of typical particles.

The purity of the ingredient aluminum is not usually stressed in its selection and purchase, except that impurities that would interfere with propellant processing or significantly reduce total combustion energy are avoided. Some of the impurities typically present are Si, Fe, Mg, O, N, C. Some of these are thought to be important in corrosion of aluminum, and may be important in combustion (primarily through their effect on the oxide coating on the particle). However, there does not



4 a



4 b

Fig. 4. Some characteristics of ingredient aluminum: a) Typical size distribution; b) Scanning electron microscope picture of typical ingredient aluminum particles.

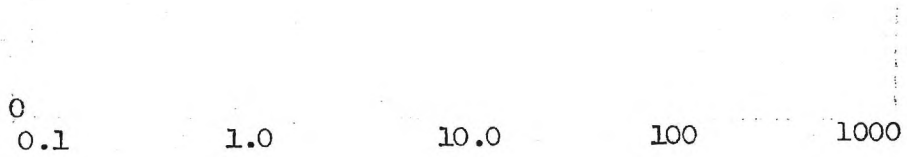


Fig. 4 a

caption

Typical Particle Size Distribution of Aluminum Powder used as a Solid Propellant Ingredient

Fig. 4 b

ption

Scanning Electron Microscope Picture of "Typical" Aluminum Particles

caption

Fig. 4 Characterization of Ingredient Aluminum

comment

Two parts of this figure should fit on one page

appear to be any definitive evaluation of the effect of impurities or additives, probably because of the unavailability of well characterized test samples. Studies have been made of alloys (particularly Al-Mg), and of aluminum with surface treatment, or with active agents added to the propellant. Results of such studies will be discussed later.

2.3 The Surface Oxide Covering Aluminum Particles

The high reactivity of aluminum assures that particle surfaces will oxidize in air - ordinarily during the manufacturing process unless measures are taken to avoid it. The properties of the oxide skin of commercial grade aluminum powder have not been the object of careful study or control, but are known to be important in die casting from powder, and have recently been found to be important to accumulation-agglomeration-ignition behavior of aluminum in propellant combustion.(R-11b)

The oxide skin is usually less than one micron thick. There is no detailed information on its crystalline state, purity, geometrical microstructure or growth processes as pertains specifically to atomized aluminum. However, a review of general literature on oxide films on aluminum is contained in Reference (R-12), which lists density of 3.96 gm/cm^3 (α - Al_2O_3) and 3.42 gm/cm^3 (γ - Al_2O_3); specific heat capacity (average for range 20-1000°C) 0.304 cal/gm; thermal expansion (average for range 20-1000°C) 8.5 x 10^{-6} deg. C^{-1}; heat conductivity 0.025 cal/cm^2 deg. C; melting point 2010 to 2050°C.

Heating of aluminum powders in controlled atmospheres has been used as a means of understanding behavior in the propellant combustion zone and suggesting ways to change behavior; such experiments are

particularly relevant to those aspects of the behavior involving the oxide "skin". It has been found (R-13) that heating of commercial powders at about 560°C in one atm of oxygen leads to weight gains amounting to about one percent of the particle weight (dependent on original particle size), followed by further slow weight increase, thereafter. It is further observed that electrical resistance through powders, high at normal temperature, drops precipitously near the aluminum melting point (Fig. 5) (R-13) suggesting breakdown of the oxide skin and metallic contact between particles. The first of these results shows that the oxide skin is not totally impermeable to diffusion of Al or oxidizing gas or at least does not remain so upon heating to 560°C. The second result shows that the oxide skin does not successfully contain the aluminum when still higher temperatures are reached - at least not in the environment of the laboratory test.

2.4 Learning About Aluminum and Using the Knowledge

From the foregoing, one might conclude that there is still a good deal to be learned about the aluminum used in propellants, and about the possibility of modifying the aluminum favorably. There is indeed much that can be learned, and the problems associated with use of aluminum (note in Section 1) suggest that some learning might be beneficial. However, the available aluminum is regarded by most of the "propellant users" as serving its purpose satisfactorily, and the logical thread between character of the ingredient aluminum and, for example, contamination of spacecraft surfaces, is indeed difficult to explain to program managers, even though it exists.

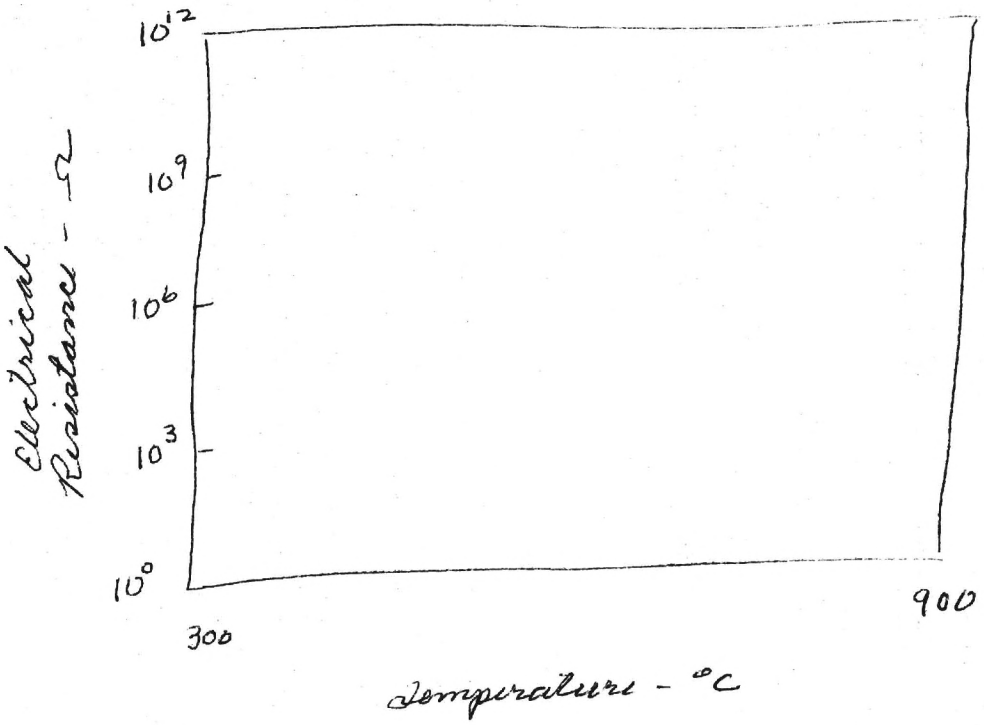


Fig. 5 Measurements of electrical resistance through aluminum powder, showing a breakdown of resistance near the aluminum melting point. This is believed to be due to diffusion or leakage of aluminum through the oxide skin, and onset temperature depends on 'quality' of the oxide skin. The same aluminum activity is believed to be responsible for sintering.

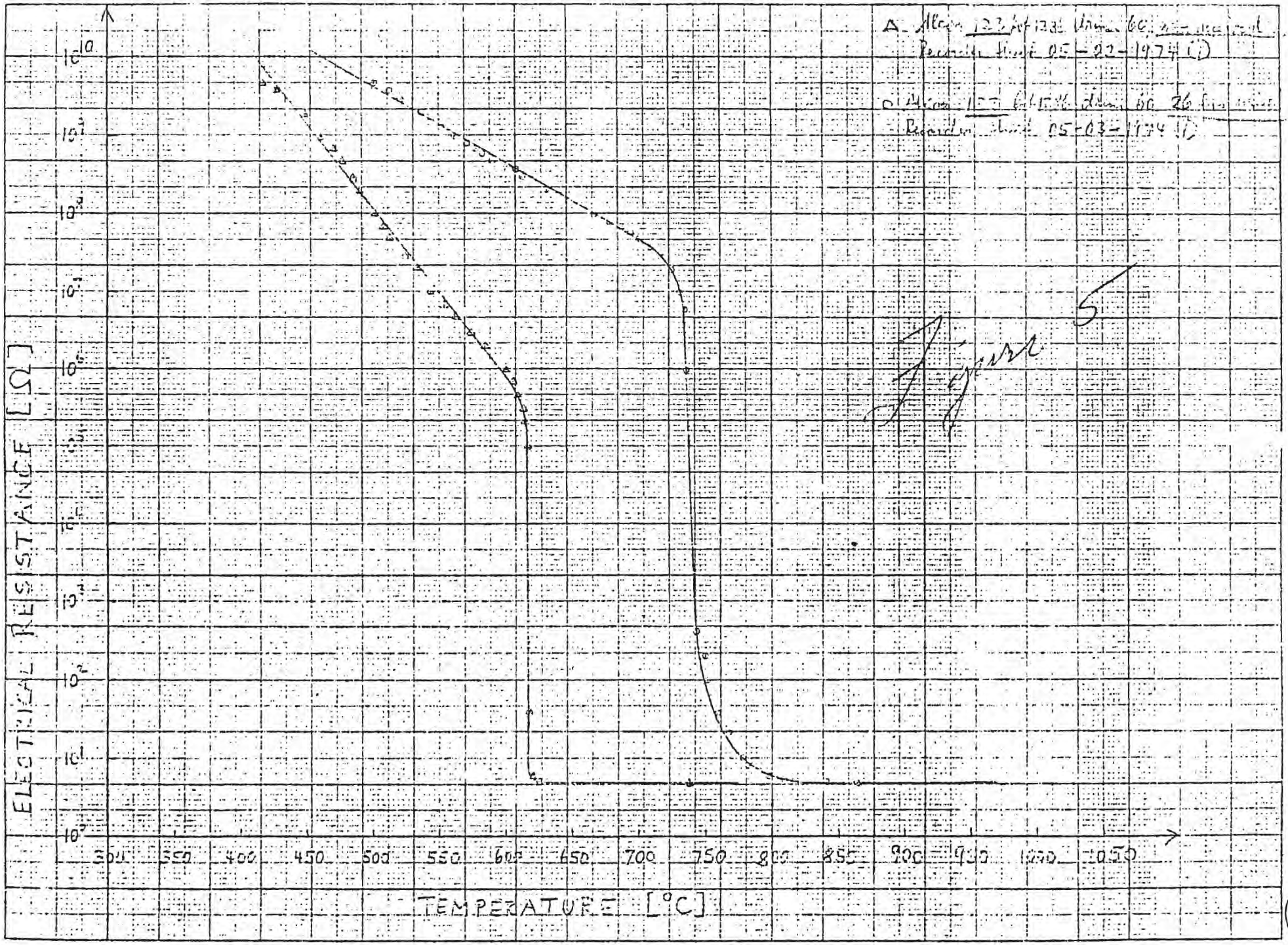

A- Alloy 133 / 133 Urea 60 2-methyl
Reading time 05-22-1974 (1)
Alloy 133 6/15% Urea 60 26 [illegible]
Reading time 05-03-1974 (1)
ELECTRICAL RESISTANCE [Ω]
TEMPERATURE [°C]
300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050

Figure 5

THE PROPELLANT MATRIX

3.1 Propellant Ingredients and Microstructure

Before considering combustion, it is helpful to examine the microstructure of the propellant, in order to understand the environment in which the aluminum will find itself when it is reached by the burning surface. The ingredient particles in the propellant are ordinarily "randomly" mixed in a binder material such as a polybutadiene rubber or a nitrocellulose-nitroglycerin colloid. The nature of the packing, and kind of neighbors of individual ingredient particles are important to the aluminum combustion, and depend on the mass ratio and particle size of ingredients. Each particle is ordinarily separated from its neighbors and surrounded by the binder to assure acceptable physical properties of the propellant. The kind of neighboring particles is affected by the fact that the particle size of ingredients in a given propellant ordinarily varies over a wide range, in order to achieve high solids loading (which is particularly desirable in order to obtain high density and specific impulse). Some simple examples of particle packing are sketched in Fig. 6a to 6e, and the examples suggest the environment of aluminum particles as they are approached by the combustion zone.

3.2 Critical Factors, Typical Situations

In examining the different situations in Fig. 6, there are a number of critical, but not obvious points to consider. First, the aluminum itself is relatively unreactive at the temperatures present

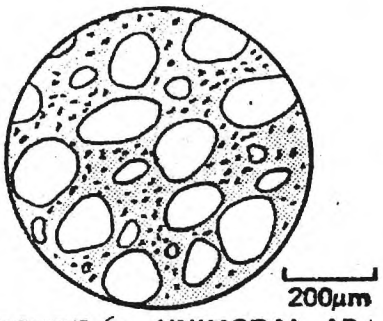


FIGURE 6a UNIMODAL AP, FINE ALUMINUM

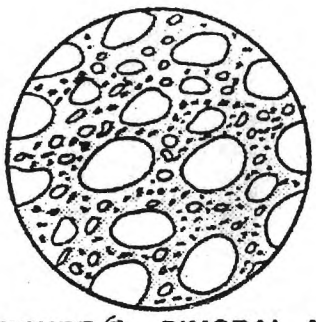


FIGURE 6b BIMODAL AP, FINE ALUMINUM

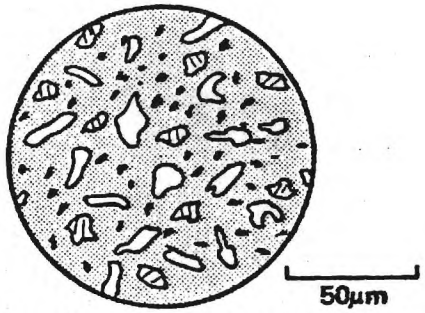


FIGURE 6c ALUMINIZED CMDB PROPELLANT WITH AP AND HMX

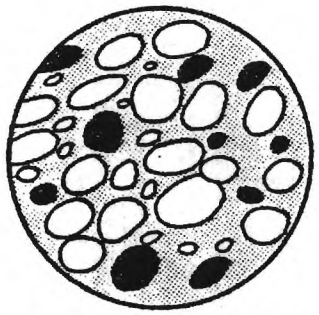


FIGURE 6d UNIMODAL AP, ALUMINUM THE SAME SIZE

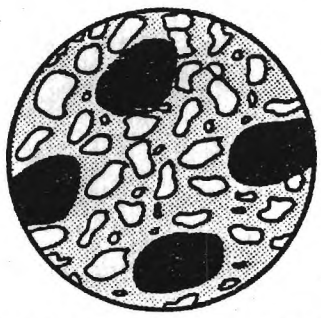


FIGURE 6e RELATIVELY COARSE ALUMINUM (OR FINE AP)

Fig. 6 Examples of Microstructure of Composite Propellants sketched as they would appear in a plane cut through a sample (in all examples the cross sectional area allocated to binder in the sketches is about double that of real propellants, in the interest of clear sketching and reproduction of the figure: open areas designate ammonium perchlorate, solid spots designate aluminum, shaded areas designate binder, cross hatched spots are HMX or other particulate ingredient)

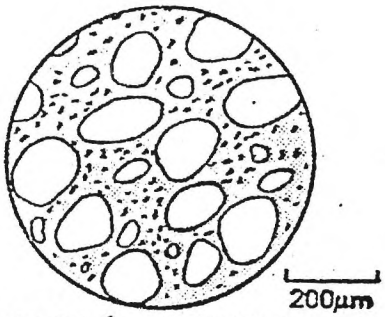


FIGURE 6a UNIMODAL AP, FINE ALUMINUM

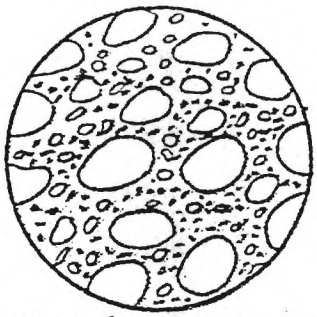


FIGURE 6b BIMODAL AP, FINE ALUMINUM

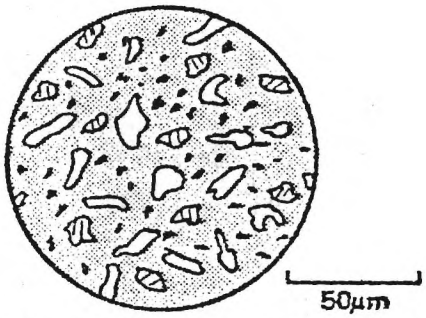


FIGURE 6c ALUMINIZED CMDB PROPELLANT WITH AP AND HMX

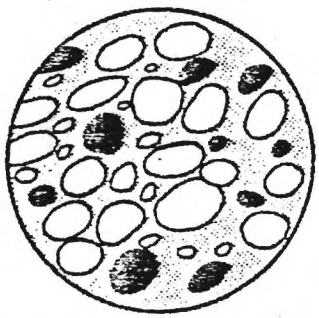


FIGURE 6d UNIMODAL AP, ALUMINUM THE SAME SIZE

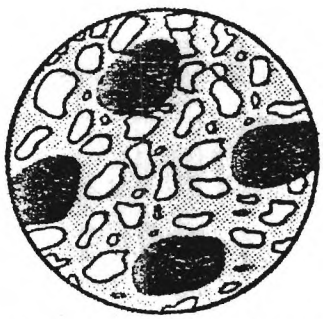


FIGURE 6e RELATIVELY COARSE ALUMINUM (OR FINE AP)

FIGURE 6

anywhere within the solid, because of the protective oxide "skin" on the particles. Second, the aluminum is surrounded by binder material; the binder or its pyrolysis products are rarely good oxidizers of aluminum or reducing agents for the oxide skin. Thus the situation is not initially conducive to aluminum reaction, a situation that applies even at the propellant surface, where aluminum particles are initially in a fuel atmosphere. Third, in some cases (fine Al, coarse AP, Fig. 6a), the aluminum is clustered in the propellant in pockets of binder between the AP particles, with oxidizer particles "remote" from most of the aluminum. This may be modified by use of a combination of coarse and fine AP, so that there are some fine AP particles intermingled with the aluminum (Fig. 6b). However, the general situation is still initially conducive to delayed ignition of the aluminum in the combustion wave for the previously noted reasons (low vapor pressure, protective oxide, non-reactive surroundings). Fourth, the AP may be a relatively minor ingredient, with considerable double base binder and/or other ingredient of lower oxidizing potential like HMX (Fig. 6c). Then the aluminum may be rather thinly dispersed through the more voluminous binder with only occasional proximity to the limited AP present. Fifth, there is the unique situation where all solid particles are of the same size (Fig. 6d). This latter situation leads to a relatively low probability that an aluminum particle will have another aluminum particle for a neighbor - or perhaps more important - a high probability that an aluminum particle will have one or more oxidizer particles as neighbors at the burning surface. A sixth situation may prevail, in which the aluminum particles

are large compared to the other ingredients (Fig. 6e). A seventh factor meriting consideration relative to environment of the aluminum is the solids-loading of the propellant: with high solids loading, proximity of most aluminum particles to an oxidizer particle is assured because of the particle size blending used to achieve favorable packing in the mixture. In this case the aluminum particles are likely to be engulfed in a hot diffusion flame as soon as the surface reaches them. These considerations are expected to be crucial as the aluminum is reached by the reaction region, as they affect the relative propensity for ignition versus surface accumulation of the aluminum.

CONDITIONS AT THE BURNING SURFACE

4.1 Surface Decomposition and "Wetness"

In the last section, the microstructure of the bulk propellant was discussed with the idea of clarifying where the aluminum was located in the structure, and where it would be located on the surface. Of course, the actual state of affairs on the surface depends on how the exposed ingredients behave in the surface environment of high temperature and reactive chemical species. Thus it is important whether ingredients melt and flow, whether they leave the surface before vaporization, whether their decomposition is endothermic or exothermic, and whether they provide an oxidative or reducing chemical environment for the aluminum. These questions will be examined in this section.

At the outset, it is desirable to note the many decomposition studies that have been made on propellant ingredients, and to consider their relevance or irrelevance to the subject of surface conditions during burning. Those studies include several tests classed as thermal decomposition experiments (Fig. 7)[R-14], and combustion experiments[R-15]. They are often supplemented by mass spectrometric measurements[R-16], high speed photography[R-17], or microscopic or chemical examination of "quenched" samples and combustion residues[R-18]. There have been many investigators who believed that propellant combustion (i.e., steady state burning) could be explained in terms of the thermal decomposition experiments[R-19], picturing ingredients as transforming independently from solid to gas in the combustion zone at rather modest temperatures, without consideration of such physical complexities as melting or

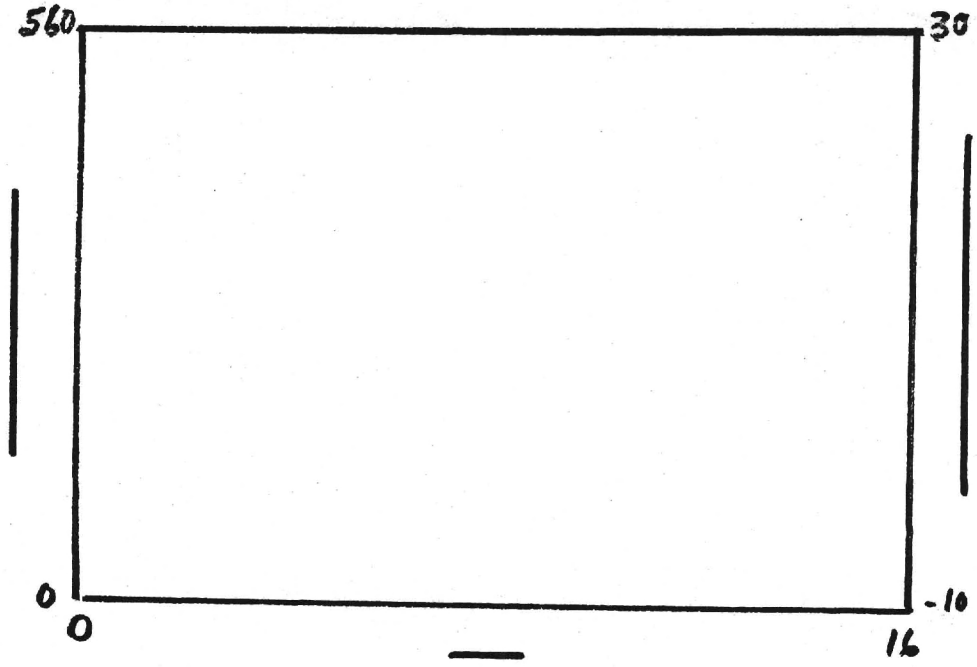


Fig. 7a Bulk decomposition of ingredients: Differential thermal analysis of ammonium perchlorate, showing crystal phase change and exothermic decomposition.

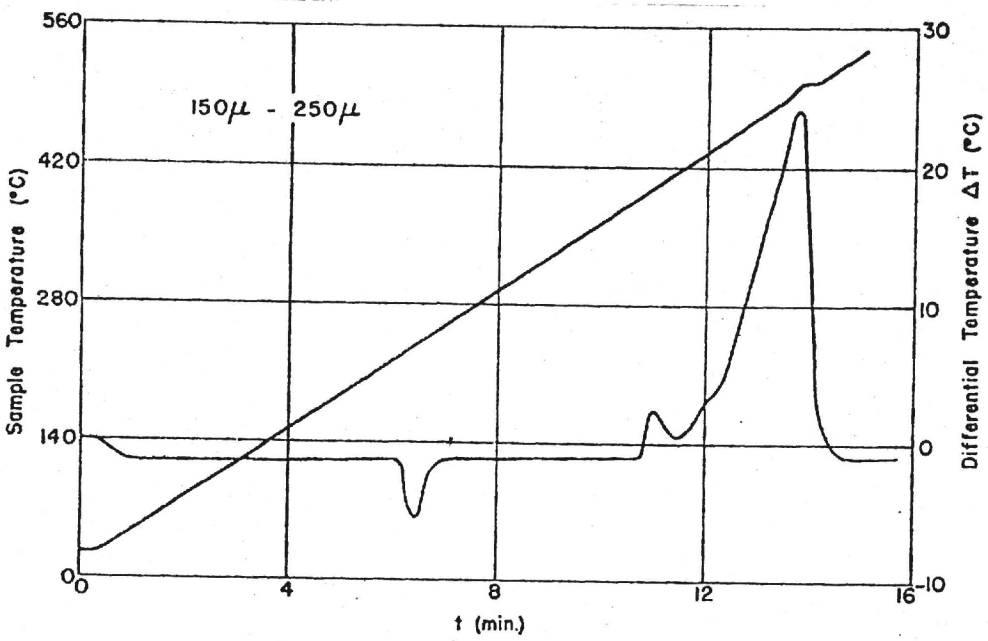

150μ - 250μ
560
420
280
140
0
Sample Temperature (°C)
30
20
10
0
-10
Differential Temperature ΔT (°C)
0
4
8
12
16
t (min.)

Fig. 7a.

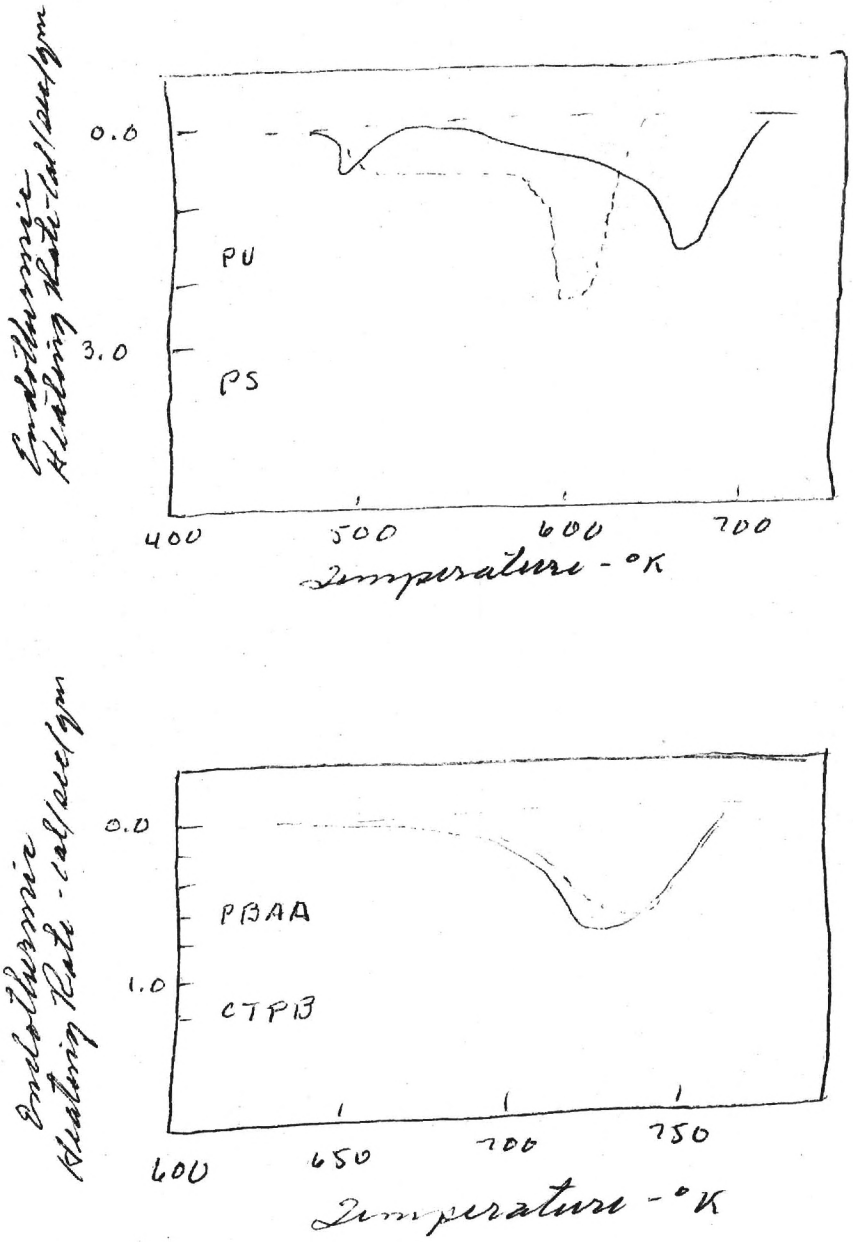
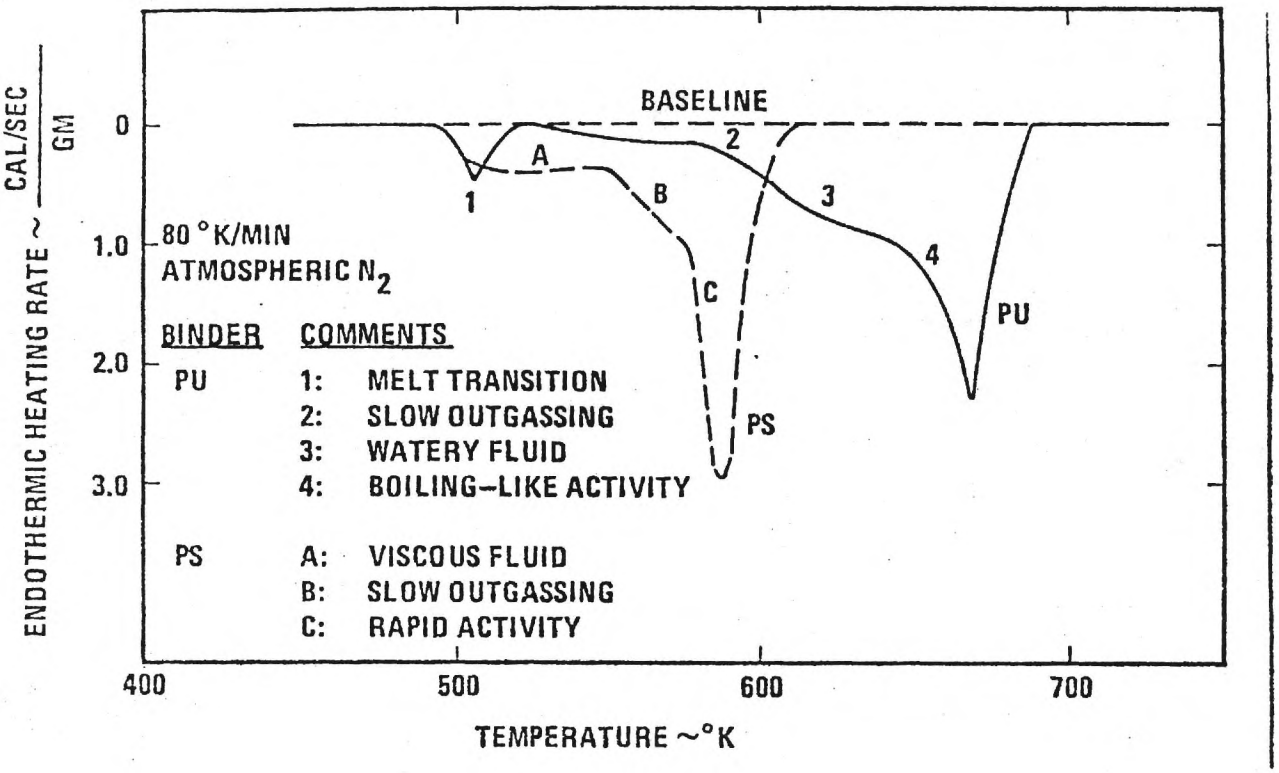


Fig. 7b Bulk decomposition of ingredients: Differential scanning calorimeter records of propellant binders and comments on physical behavior from companion tests in hot stage microscope.



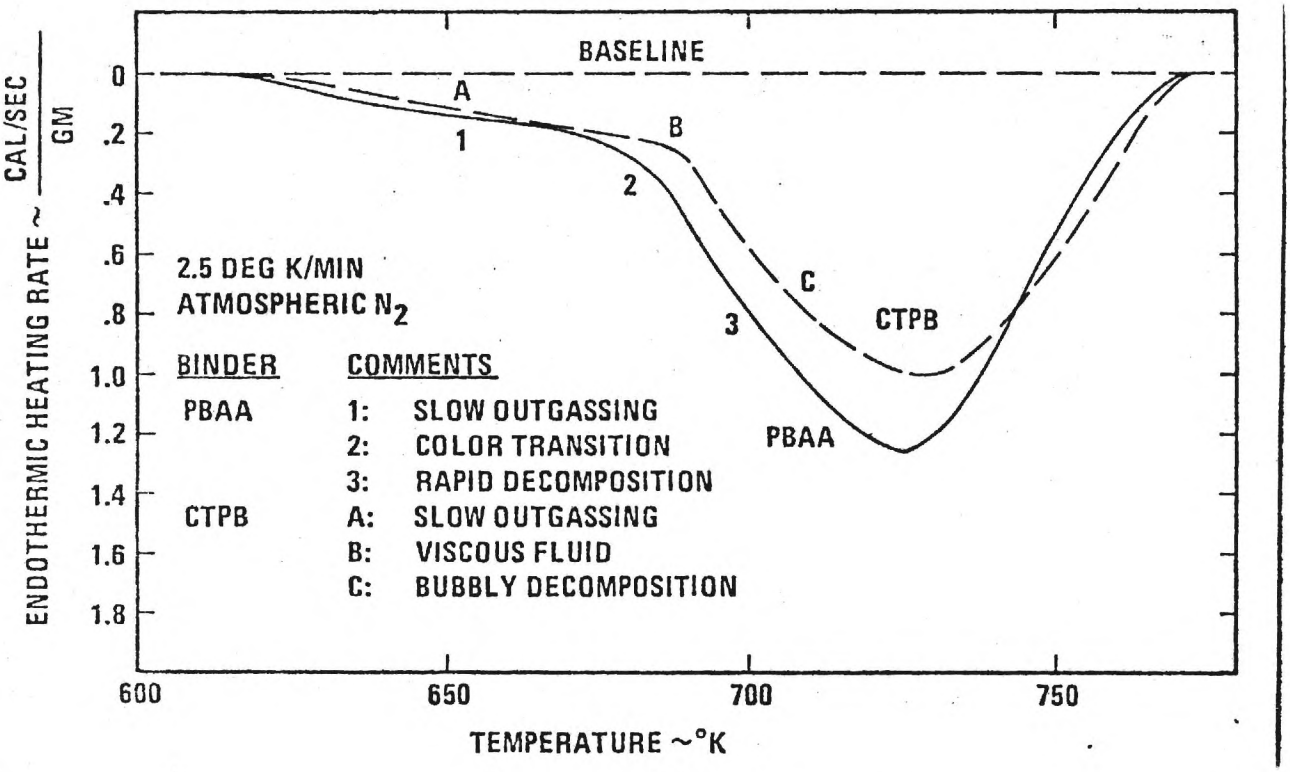


Fig. 7b. ~~Complexity of the Decomposition of Binders (Curves are from Differential Scanning Calorimeter)~~

accumulation of intermediate or final products on the burning surface. In the case of an unaluminized propellant, this would imply a burning surface that reflected the microstructure of the propellant matrix (Fig. 6), with more rapidly decomposing ingredients recessed below the mean surface, and more slowly decomposing ingredients protruding above the mean surface (Fig. 8a). In practice surfaces of this kind are observed (Fig. 8b), but the oversimplification of the ingredient decomposition model is indicated by the dependence of the surface microstructure on pressure, catalysts and particle sizes in ways not predictable on the basis of low temperature decomposition characteristics alone. More specifically, the question of which ingredient protrudes and which is recessed depends not only on decomposition characteristics, but also on flame zone structure (Fig. 8d).

A more careful look at the decomposition of ingredients has been made in recent years, and it is observed that decomposition is far more than a gassification at the surface. It has long been known that some oxidizers (e.g., ammonium nitrate) melt, and it is reasonable to assume that decomposition in the melt will produce a solution of melt and products, very likely containing bubbles of gaseous products. Ammonium perchlorate has been observed, contrary to earlier reports [R-20], to have a very complex surface during decomposition (Fig. 9) [R-21] and self deflagration (Fig. 10a) [R-22] with evidence of a liquid surface during deflagration. Potassium perchlorate is observed to burn with accumulation of liquid KCl product on the surface, a phenomenon observed even with potassium-doped ammonium perchlorate crystals (Fig. 10b) [R-23]. Most binders exhibit molten surfaces, (Fig. 7b, 11), even during slow decomposition experiments. The binder apparently breaks down in steps, [R-24] with concentrations of the more

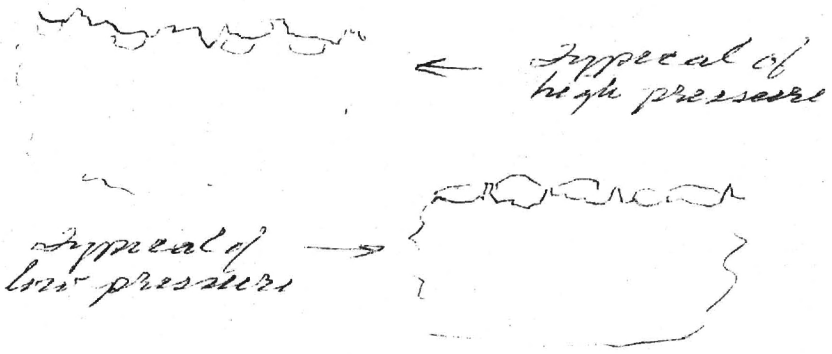


Fig. 8a Slowly decomposing ingredients protrude above the mean surface.

Figure 8 Burning Surface and Combustion Zone Structure (non-aluminized propellant).

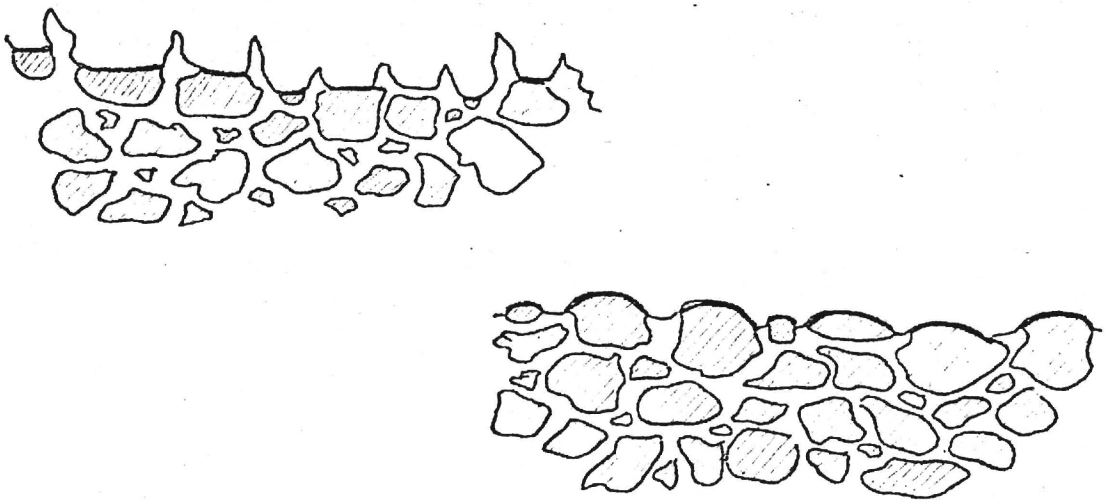
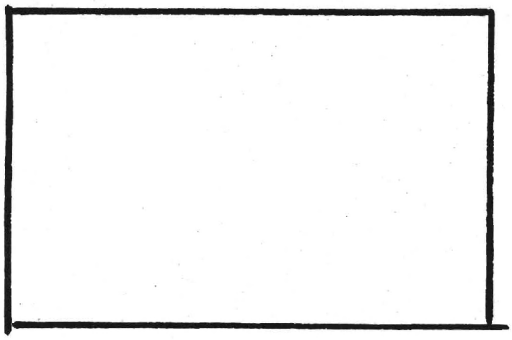
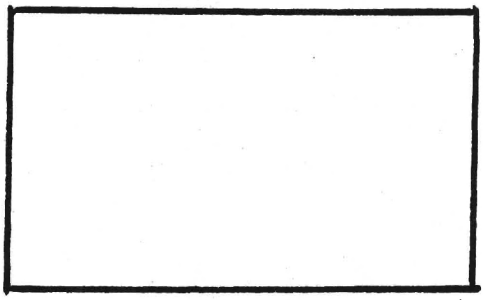


Fig. 8a

Fig 5a



Quenched from
1000 psig



Quenched from
150 psig

Fig. 8b Surface structure of samples quenched at different pressures.

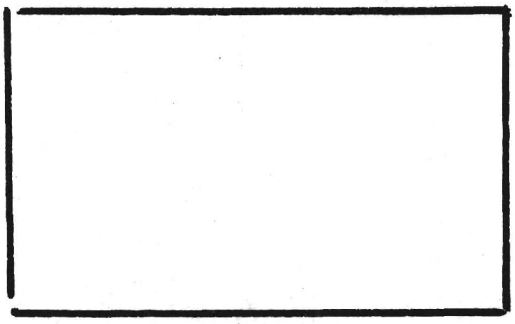
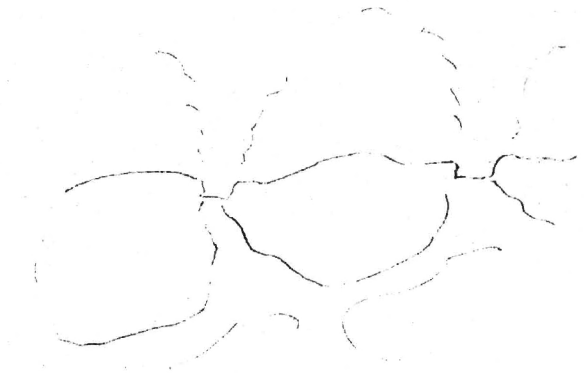


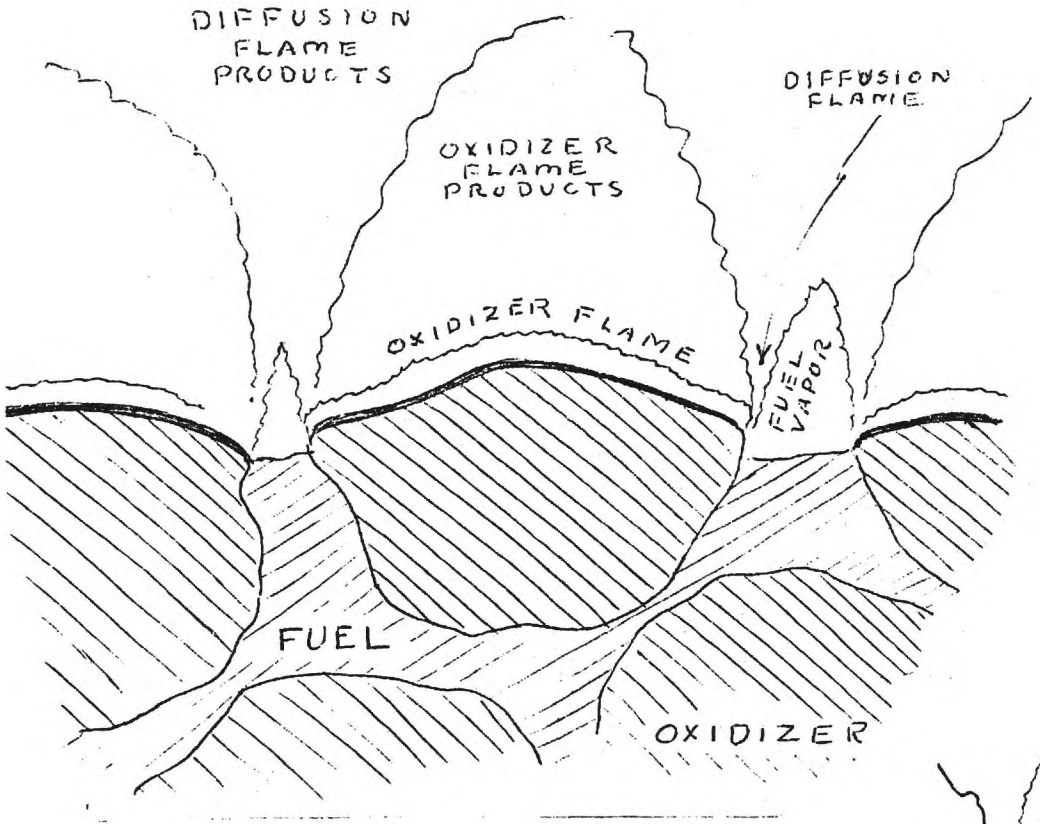
Fig. 8c Propellant internal microstructure as revealed by a cut face.



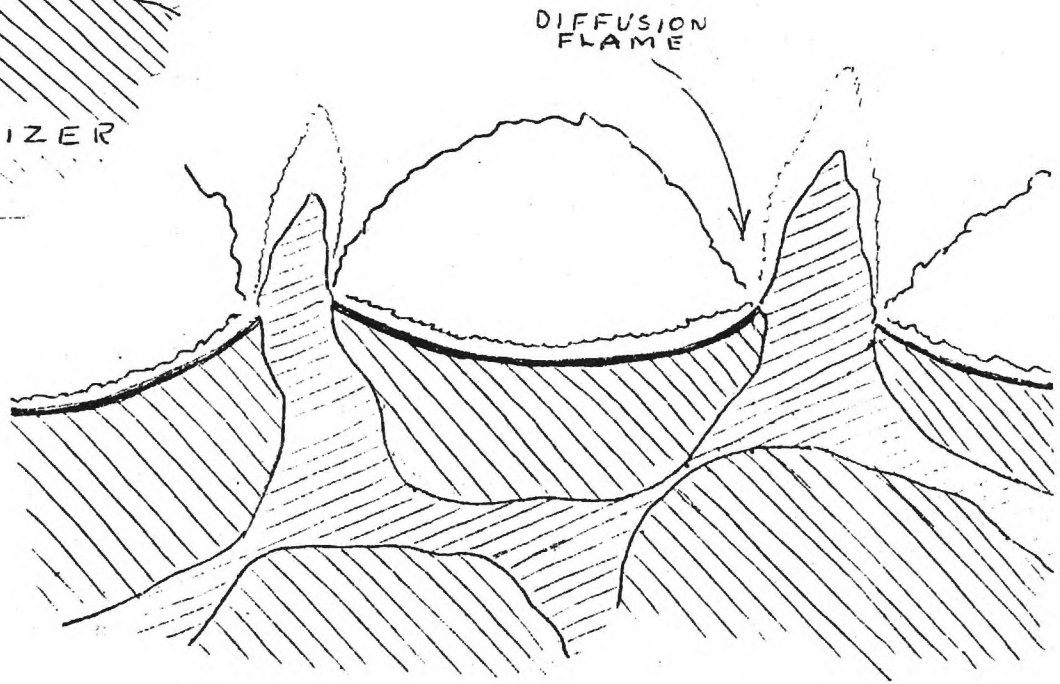
Low Pressure, AP Dominates

High pressure, Binder Dominates

Fig. 8d Sketch describing the structure of the gas phase combustion zone.

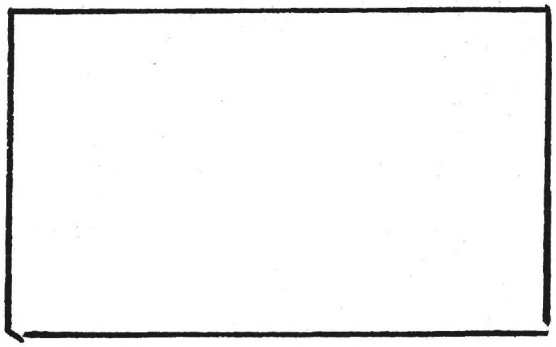


Low pressure, AP protrudes

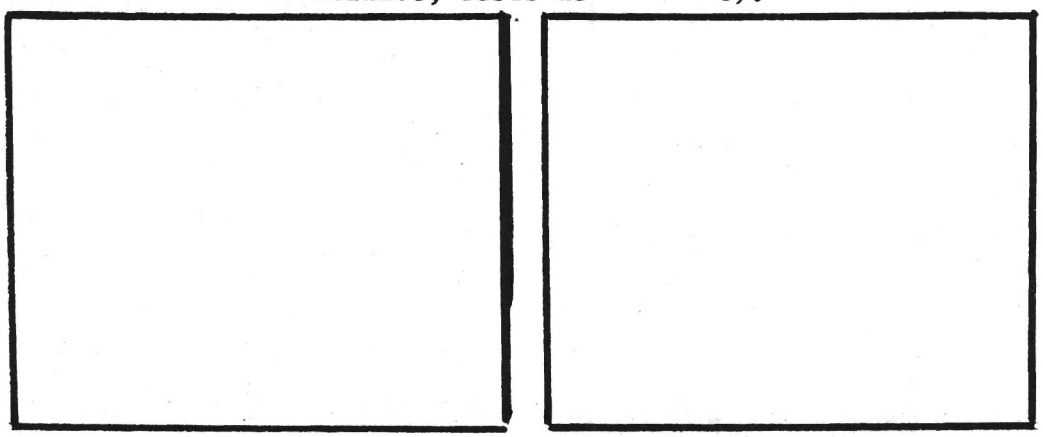


High pressure, binder protrudes

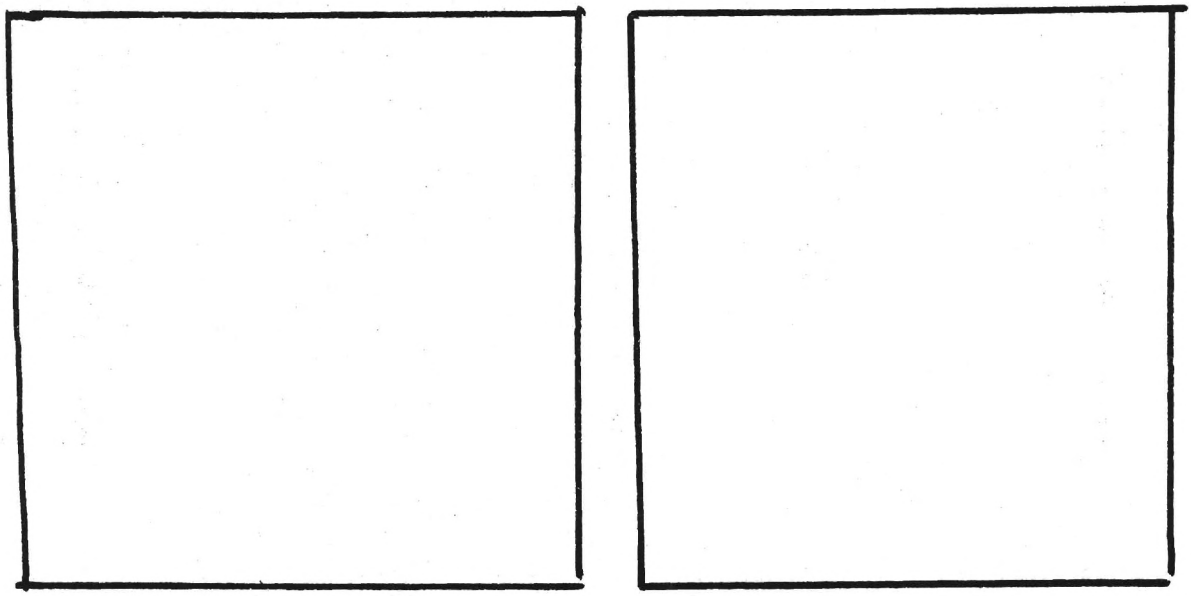
Fig. 8d ~~The burning surface of an ammonium perchlorate-hydrocarbon binder propellant~~



9a Decomposition sites on the c - face of AP single crystal (focus is on the surface, tests at °C).

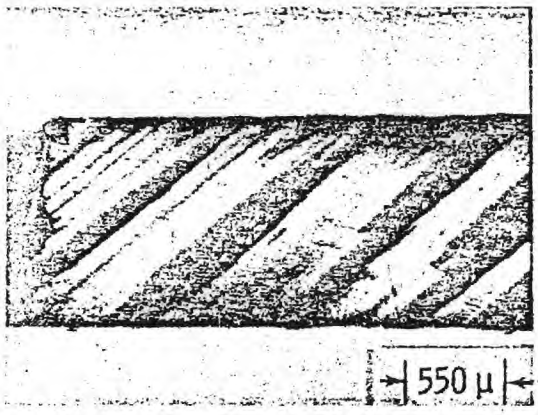


9b Decomposition sites at higher magnification, on the m - face (scanning electron microscope picture, tests at °C).

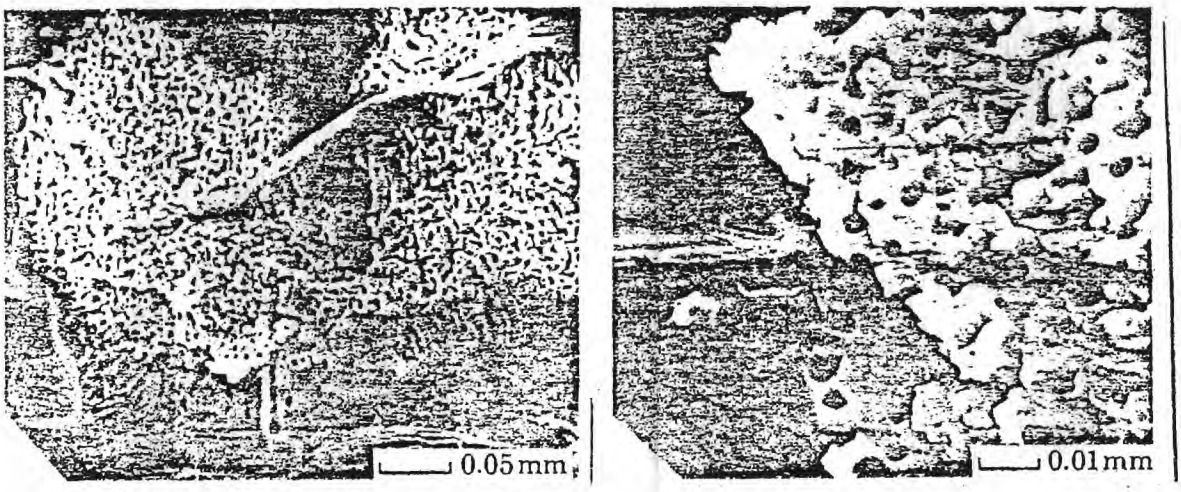


9c Surface of AP spheres after partial sublimation at °C (scanning electron microscope pictures).

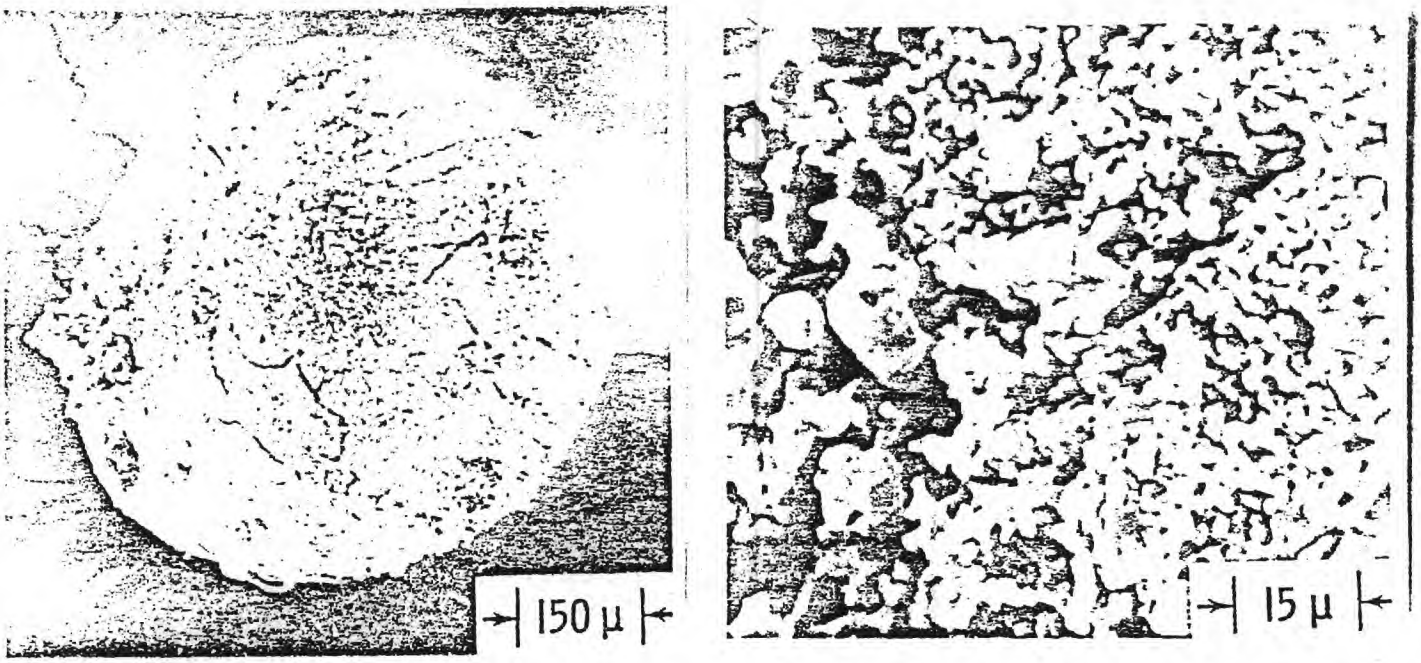
Fig. 9 Complexity of Decomposition of Ammonium Perchlorate



PART a Decomposition sites on c-face of AP single crystal; focus is on surface.



PART b Scanning electron microscopy.
Appearance of product in a plane parallel to an *m* face (× 220).
The residue under higher magnification (× 1100).



PART c Scanning Electron Microscope Photographs of Ammonium Perchlorate After Beginning Sublimation

Fig. 9. Complexity of Decomposition of Ammonium Perchlorate

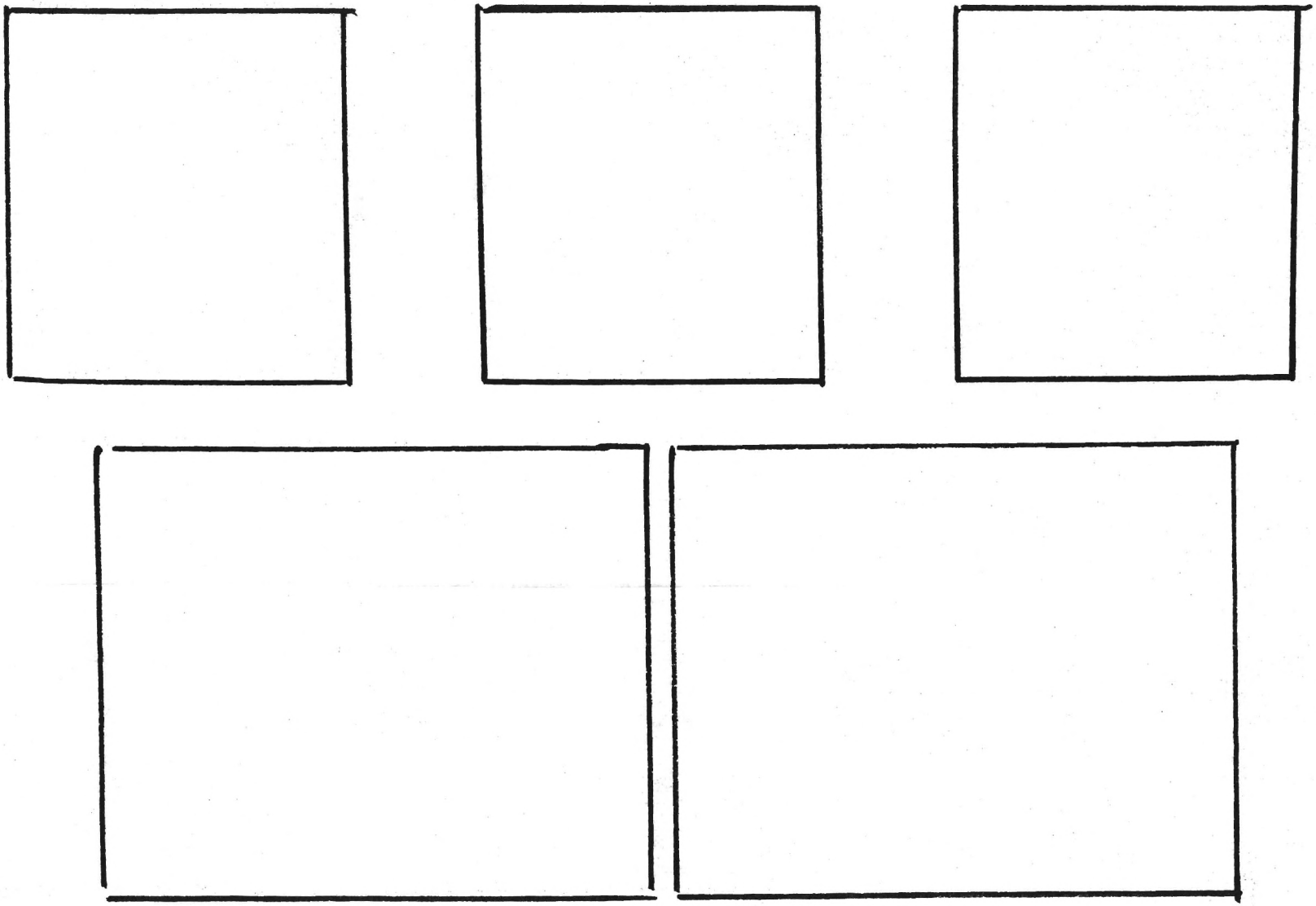
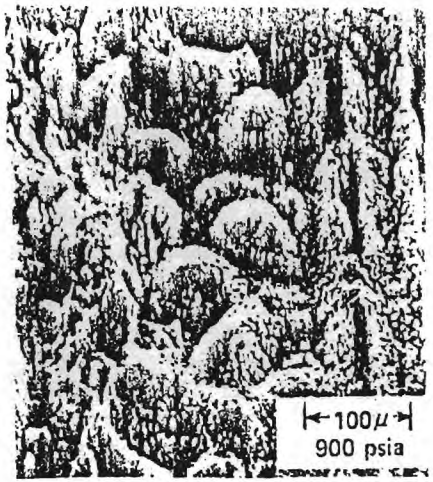
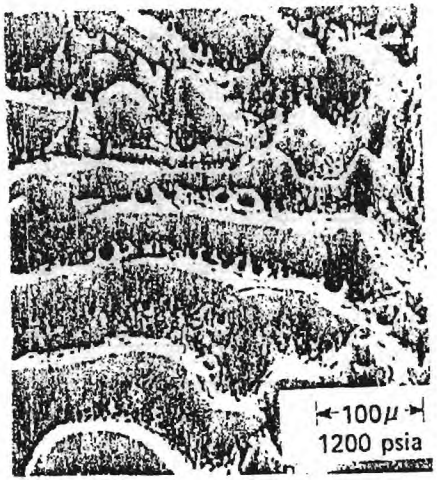
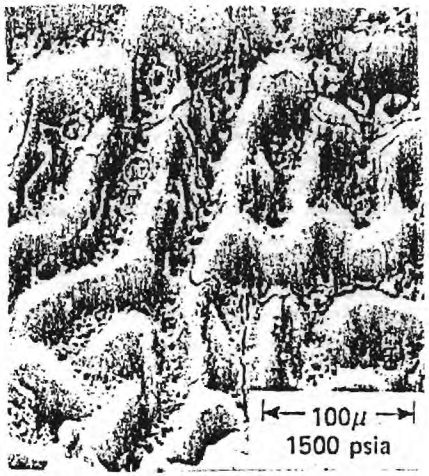


Fig. 10a Top, surface pattern on deflagrating AP crystals at three pressures (SEM's of samples quenched by rapid depressurization); Bottom, details of quenched surfaces, showing evidence of a liquid layer.

Fig. 10 Complexity of Deflagration of Ammonium Perchlorate







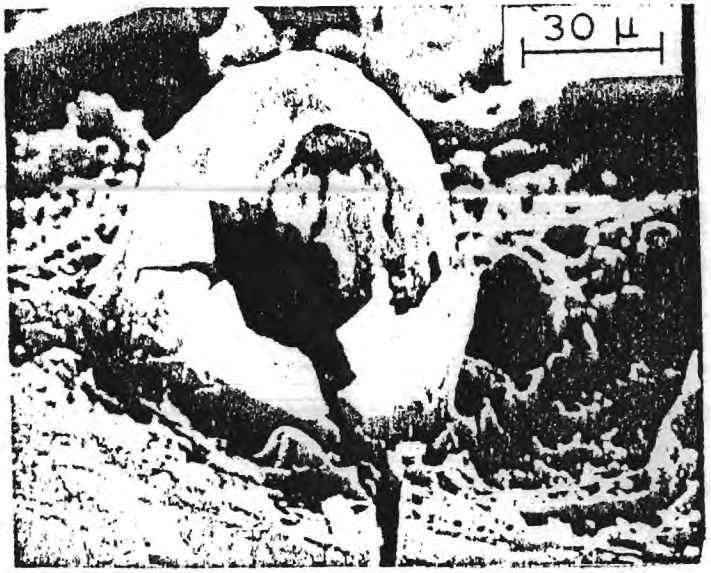


Figure 10 a

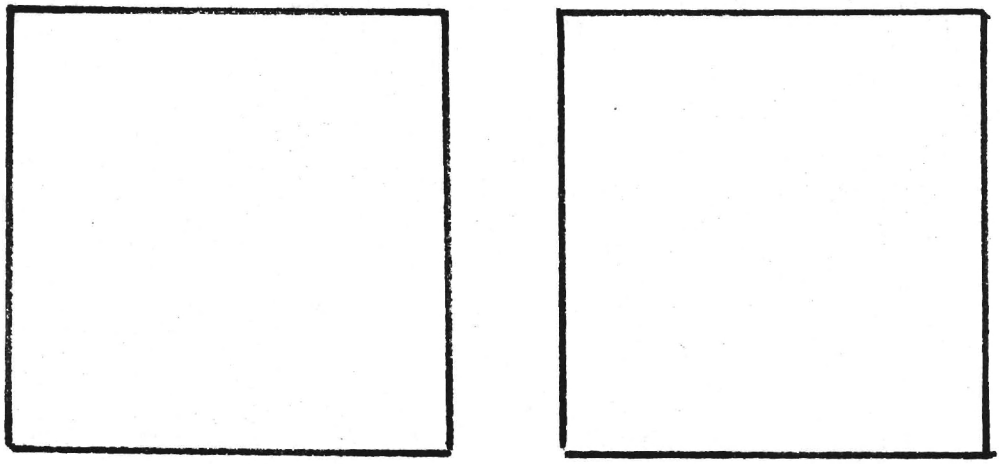
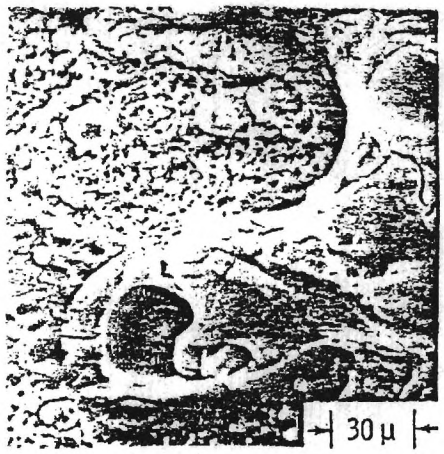


Fig. 10b Quenched surfaces of impure crystals; on left, AP doped with 0.8% K^+, quenched from 600 psia; on right, AP dped with 0.015% Cr_2O_7, quenched from 2500 psia. These samples illustrate the tendency for accumulation on the burning surface.



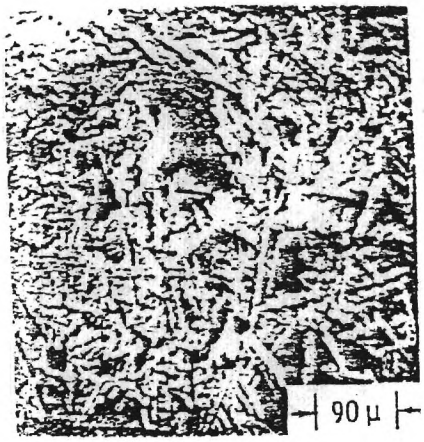


Fig 10 b

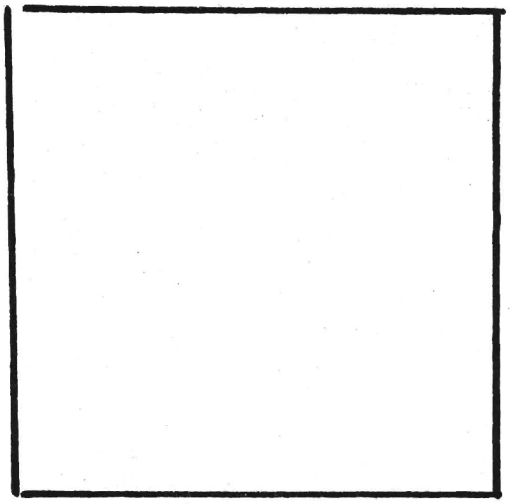


Fig. 11 Evidence of binder flow, manifested by quenched sample consisting of a binder layer sandwiched between 2 sheets of AP.

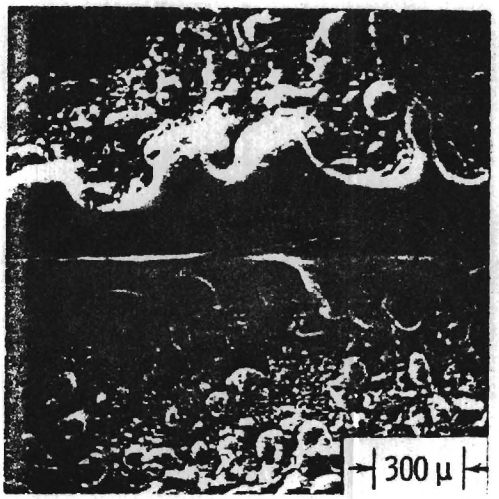


Figure 11

stable intermediate products and chars on the surface. Except in the case of ammonium perchlorate, the effect of addition of burning rate modifiers on these processes has been only superficially examined. The modifiers tested with AP accumulated on the surface of the crystals (Fig. 10b)(R-25).

In terms of aluminum behavior, a burning model based on simple gassification of surface ingredients would imply that when aluminum particles are present, they would emerge at the binder surface and (being incapable of decomposition and not hot enough to evaporate) float away in the binder pyrolysis products. The surrounding binder product flow is usually a poor oxidizer or a non-oxidizer, so most aluminum particles would not ignite until they encounter more favorable temperatures and oxidizing atmospheres in the diffusion flame. The most conspicuous difference between this "idealized" picture of aluminum behavior and the real behavior is implicit in the more sophisticated view of the ingredient pyrolysis with surface wetness and accumulation of products described above. Given these conditions it is reasonable to expect that the aluminum particles will not depart the surface immediately, their behavior instead depending on their own nature, the nature of the other surface materials, the nature of the surrounding gas, and the temperature.

4.2 Surface Temperature and Aluminum Heating

As the burning surface of a propellant approaches any one aluminum particle, the particle temperature starts to rise. Under typical conditions (burning rate 10^4 μm/sec), the temperature rise in the solid (from 1/2 of the total rise, up to the surface temperature) occurs in 1.5 msec in a

layer 15 μm thick (less at higher burning rate). Thus, an aluminum particle is of the same order of size as the thermal wave.

Protected by its oxide "skin" and non-oxidizing fuel environment, the aluminum simply absorbs heat as the burning surface approaches. A simplified calculation[R-26] (applicable to fine particles in a thick thermal wave) shows that the aluminum temperature remains close to that of the surrounding material in the thermal wave; larger particles (for which the calculation is not quantitatively valid) are predicted to have a temperature lag. The calculations are helpful in visualizing the aluminum particle heat-up, but one must keep in mind the complexity of the burning surface, in which emergence of the aluminum particles may occur in a three-dimensionally complex burning surface with protruding or recessed surfaces of aluminum-loaded binder, with particles that may be dimensionally of the same order as the thermal wave or binder element.

Because of geometrical complexity and rapidity of temperature change, it is difficult to define any precise thermal environment for the aluminum. As indicated above, the particle sees a rapid temperature rise in the solid and emerges at the surface in a film (usually) of molten binder and/or intermediate decomposition products. At this point it becomes exposed to high heat flux from the flame zone. The subsequent temperature history is a matter of speculation, presumably dependent on location of the particle relative to the diffusion flamelets (Fig. 8d) and oxidative species. A useful reference point for discussion of temperature effects on the aluminum is the surface temperature of the propellant, and its value relative to the melting point of the aluminum (660°C). Hydrocarbon binders have surface temperatures of roughly 575 -

700°C, value depending on type of binder, type of measurement, and burning rate (surface heating rate)[R-27]. Some binders (e.g., fluorocarbon, polymide) exhibit much higher surface temperatures, and the nitrocellulose-nitroglycerin binders exhibit lower surface temperatures in the 350 - 400°C range[R-28]. Ammonium perchlorate surface temperatures are apparently in the vicinity of 600°C[R-29].

Because of the poorly determined, ingredient-dependent value of the surface temperature, and because of the thermal lag in heating the aluminum particles as they are approached by the burning surface, no general statement can be made as to whether the aluminum is solid or molten when it emerges at the burning surface. Either situation might pertain, depending on the variables noted above. One might anticipate that this would be an important question, and it will be discussed in later sections, where the behavior of the aluminum during its residence on the surface is discussed.

4.3 Consequences of Surface "Wetness"

One of the originally unexpected aspects of behavior of aluminum in solid propellant combustion was the tendency for agglomeration into large droplets. The processes governing this behavior, discussed in the next section, are not yet fully understood. However, one prerequisite to agglomeration is the opportunity for aluminum particles to come in contact with each other. It has been suggested that this opportunity arises from mobility of aluminum relative to the burning surface[R-30], although it is not clear why such mobility would lead to surface-wise motion rather than escape from the surface. Actually, the "wetness"

of the surface dictates that aluminum particles will be temporarily retained there by surface tension, giving rise to the opportunity for accumulation in situ. Combustion photography and quench-burn tests give decisive evidence of such accumulation, with the aluminum distributed on the burning surface (Fig. 12) in a pattern indicative of the original distribution in the binder (Fig. 6, 8). This accumulation of aluminum sets off a complex chain of events that dominates aluminum combustion.

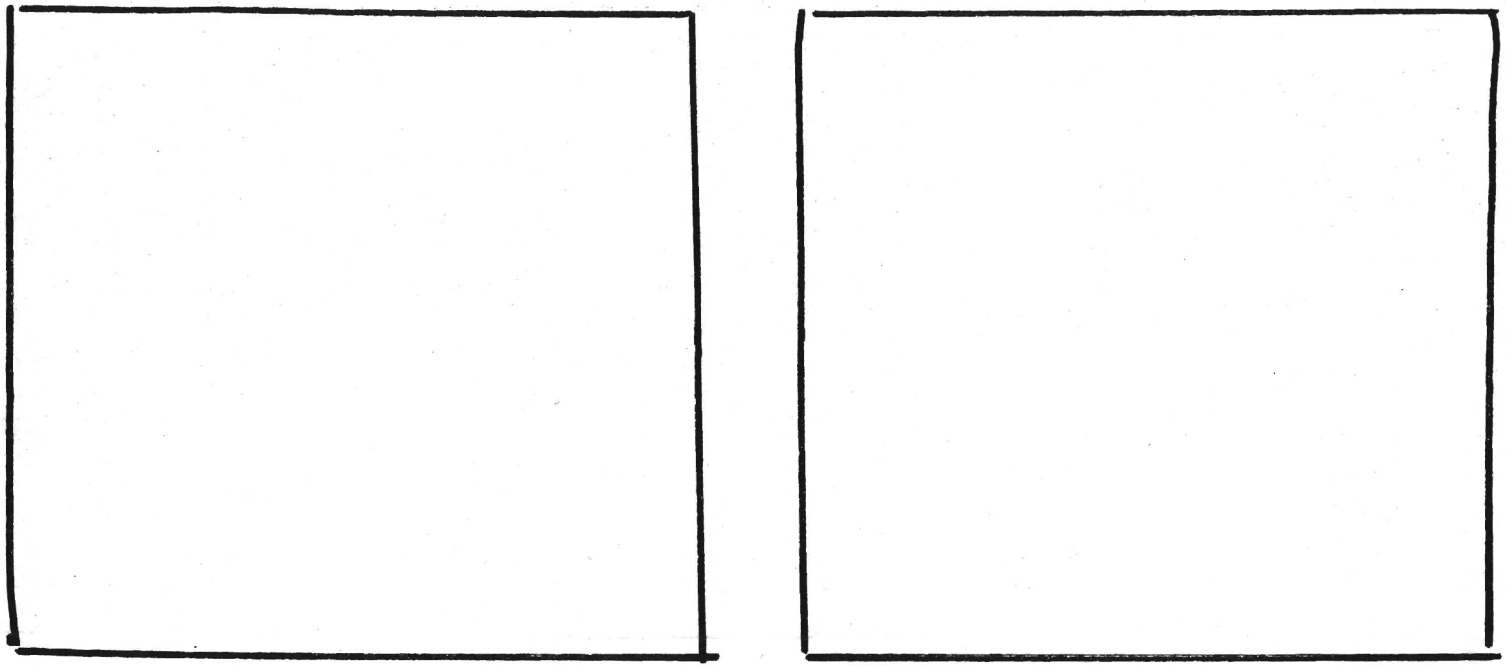


Fig. 12 Array of aluminum particles in the binder around the larger oxidizer particles (surface quenched by rapid depressurization).

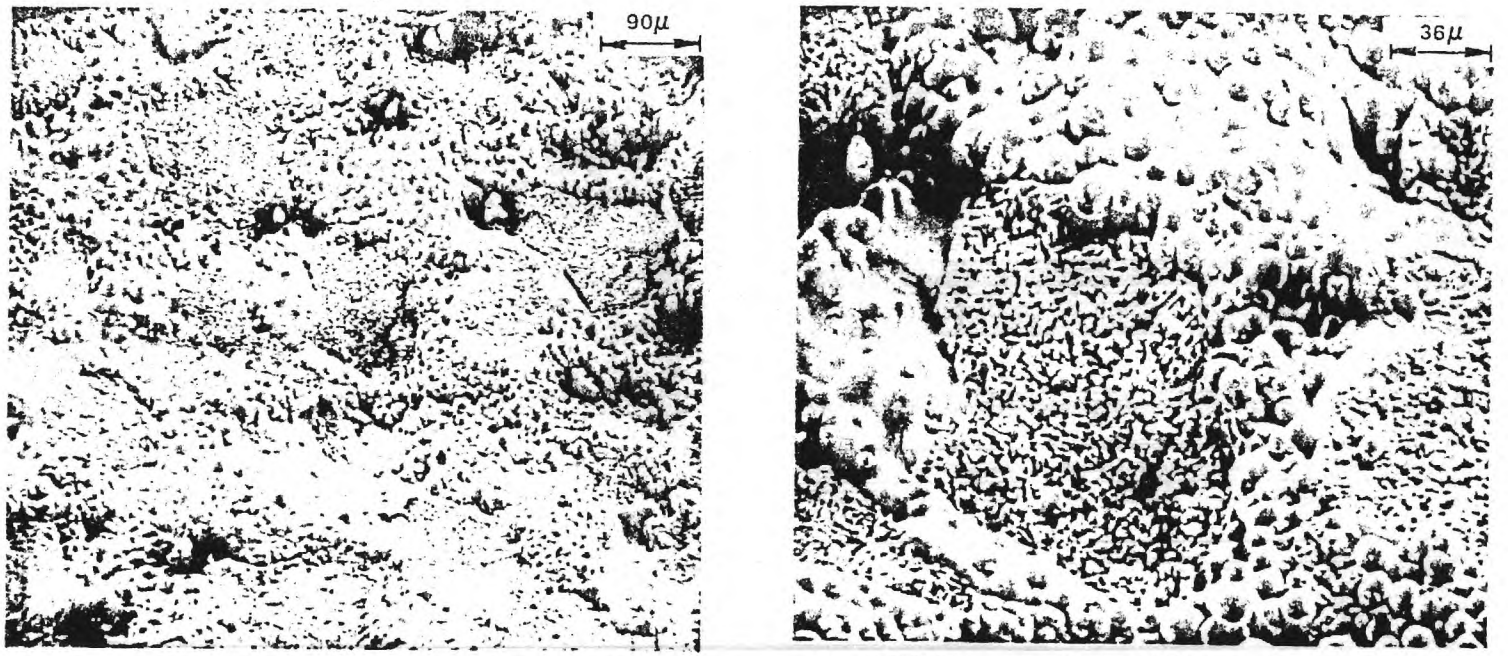


Fig. 12. ~~Quenched Surface of an Aluminized Propellant Showing the Pattern of Accumulating Aluminum Particles in the Binder, Surrounding the Larger Oxidizer Particles~~

ALUMINUM BEHAVIOR ON THE BURNING SURFACE

5.1 Kinds of Surface Behavior

Given the surface retention of aluminum particles and surface conditons described in the foregoing, a variety of processes become possible, many of which are revealed by combustion photography (e.g., Fig. 1, 13, 14 (R-31)). In the simplest case, typical of propellants with low aluminum concentration, the particles linger briefly and then depart the surface. When the aluminum concentration is higher, the surface-attached particles are joined by other emerging particles. Then the particles tend to stick together by either adhesion or cohesion (see App. A for terminology). This leads to an appreciable concentration of aluminum on the burning surface, in the form of an interconnected layer of filigree (Fig. 12). The accumulation may form into recognizable fragments of interconnected particles, referred to here as "accumulates", (App. B), which tend to adhere for a time to the surface with varying degrees of mobility. Eventually the accumulates melt down into burning "agglomerates", (App. B), either on the burning surface or after leaving the surface. Fig. 15 outlines the different paths that an aluminum particle may follow in the foregoing evolution from emerging particle to burning droplet.

It is particularly instructive to note two features of the "progress chart" in Fig. 15: a) the experiences of any aluminum particle on the surface are sequential (although not all identical), and b) the chart tells very little about the mechanistic basis for

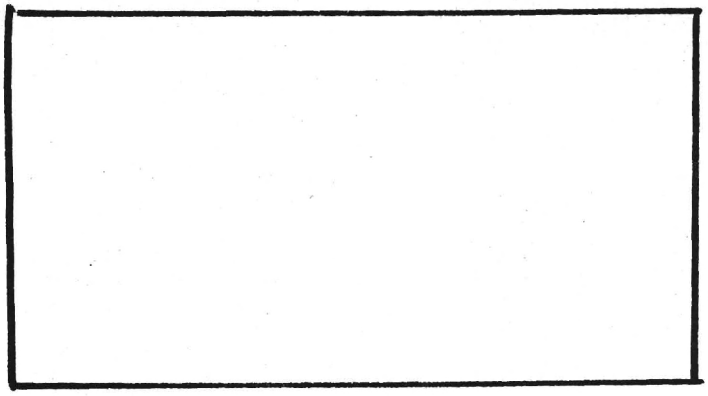


Fig. 13 Accumulated aluminum as shown by combustion photography -- note the loosely attached filigree.

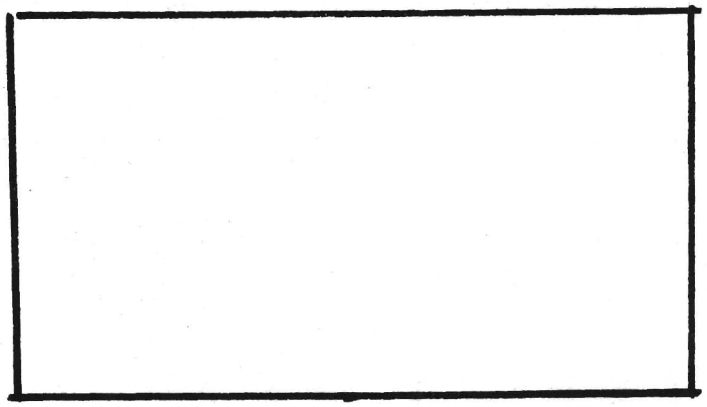


Fig. 14 Accumulated aluminum as shown in combustion photography -- note the crust-like layer, which is seen from the movie sequence to be rigid.

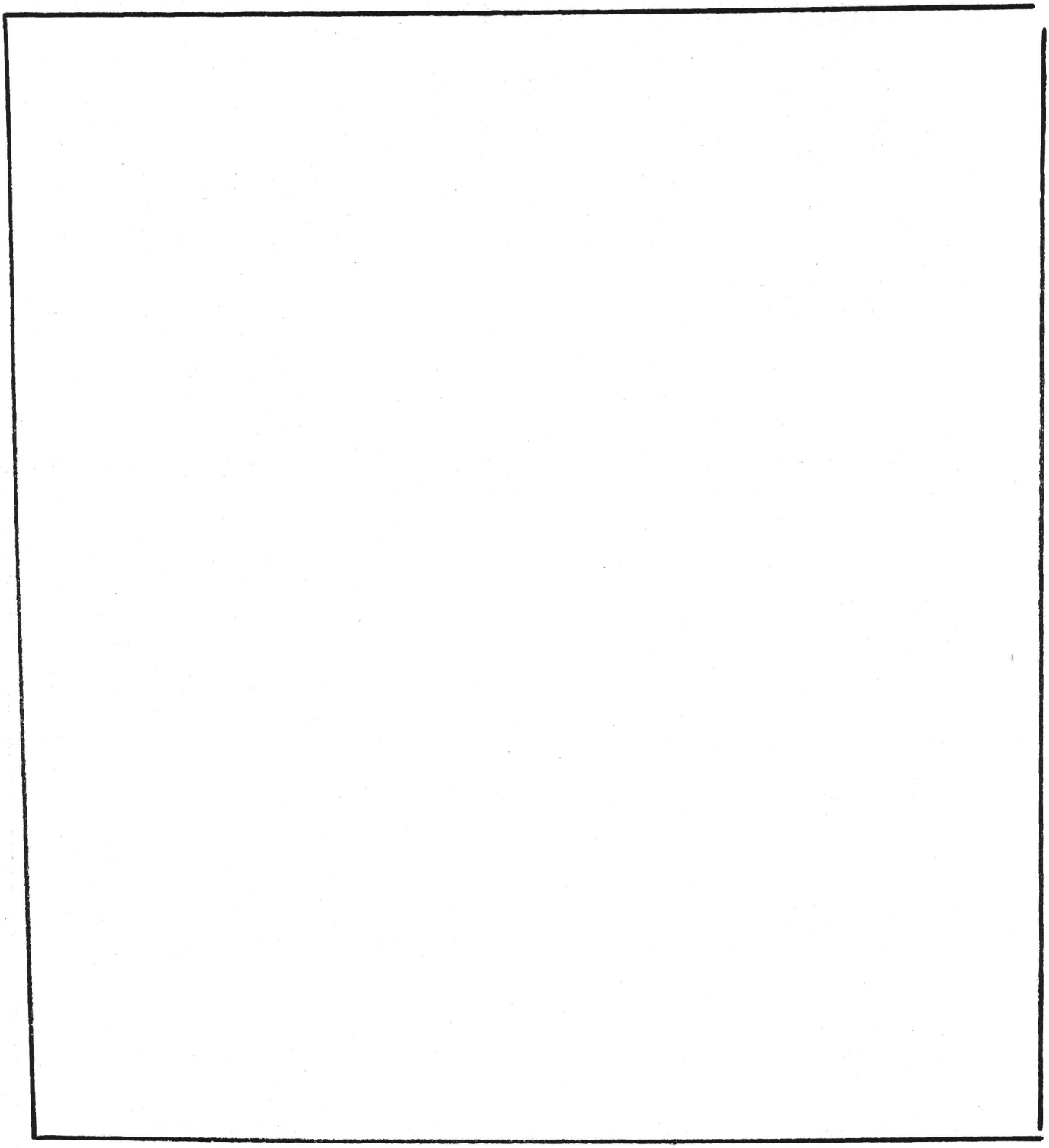


Fig. 15 Sequence of aluminum behavior in the solid propellant burning surface.

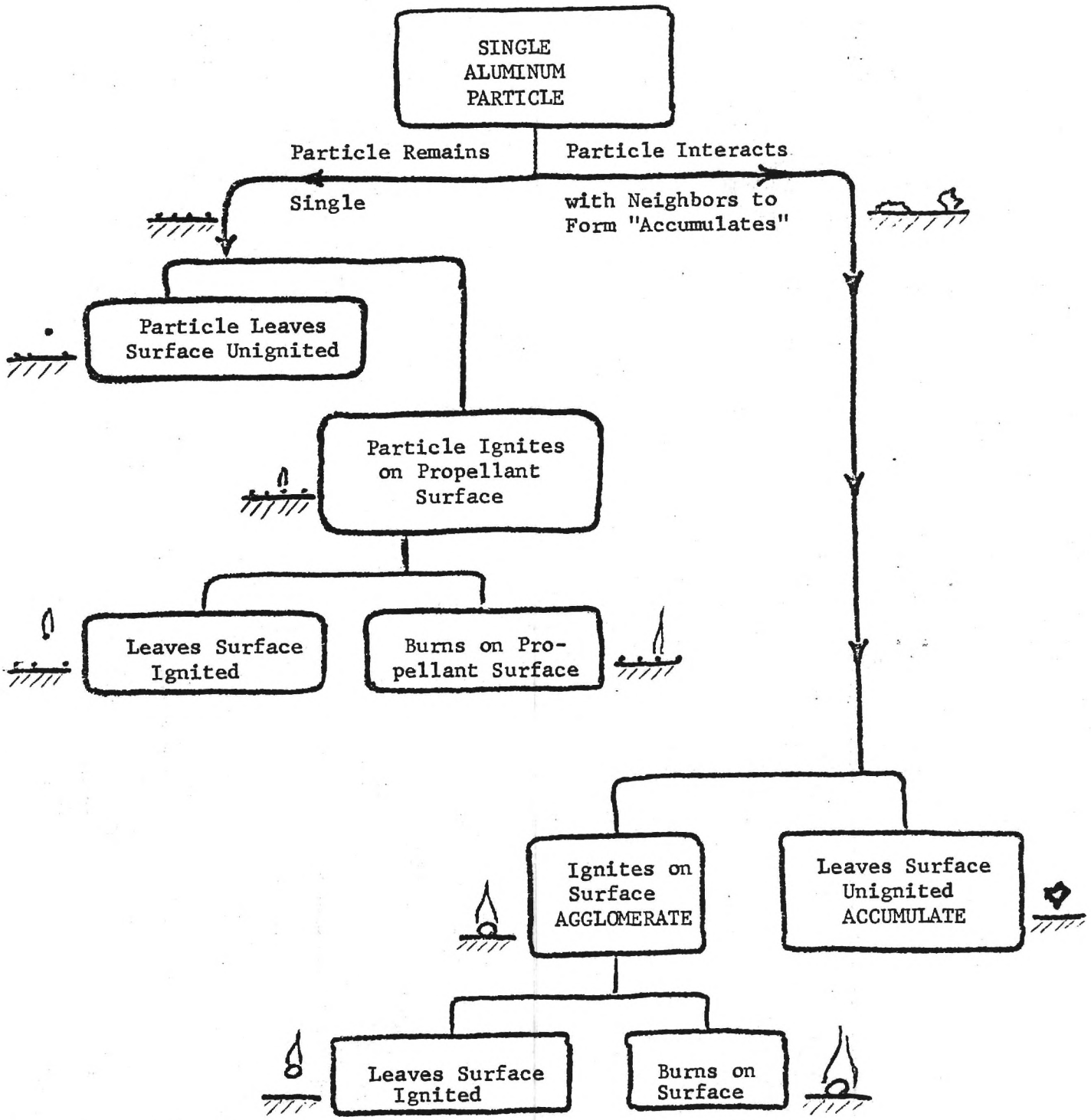

SINGLE ALUMINUM PARTICLE
Particle Remains Single
Particle Interacts with Neighbors to Form "Accumulates"
Particle Leaves Surface Unignited
Particle Ignites on Propellant Surface
Leaves Surface Ignited
Burns on Propellant Surface
Ignites on Surface AGGLOMERATE
Leaves Surface Unignited ACCUMULATE
Leaves Surface Ignited
Burns on Surface

Figure 15

the steps in the sequence. The first of these features and Fig. 15 imply that the aluminum particle may experience a wide range of conditions, situations, and changes while on the burning surface; and that all aluminum particles will not follow the exact same sequence, even in combustion of a single piece of propellant (because they are not all similarly located in the propellant microstructure).

The second of the features of the progress chart (Fig. 15) stressed above follows from the heavy reliance of present knowledge on the experimental method of combustion photography, which does not produce fundamental (detailed) information about ingredient behavior and combustion zone structure. In the following, aluminum behavior on the surface will be described from photographic observations, but will also be explained in-so-far as available information from other types of observations permits. Because of the paucity of fundamental information, the explanations may not be satisfyingly unequivocal; but the present situation has a need for explanations, even though some of the explanations merit only the rank of hypotheses.

5.2 Propellant - Combustion Zone Microstructure and Accumulation of Aluminum

In Section 4 the surface configuration of burning unaluminized propellants was illustrated by photomicrographs of quenched surfaces, a subject discussed also in many other references, (R-32). The sketch in Fig. 8 describes the appearance of burning surfaces of unaluminized propellant in profile. Although quench testing of aluminized propellants has been less extensive, the collective results of sources of information

suggest that the burning surface progresses in the manner sketched in Fig. 16, (particularly for propellants with microstructure such as in Fig. 6a). The aluminum accumulates on the binder surface as seen in Fig. 12. The pattern of the accumulation conforms to the presence of binder underlying the aluminum, although under unfavorable combustion conditions (e.g., low pressure, low oxidizer content) the aluminum may overlie the entire burning surface ((Fig. 13, 14; (R-31)). The preference for accumulation of aluminum on the binder surface is of course due first of all to the fact that the aluminum is contained in the binder in the original mix, i.e., it is in binder when reached by the surface. The fact that surface retention occurs in the binder leads to accumulation there, and explains the earlier preoccupation with the surface wetness that causes the retention. These observations in turn explain why the distribution of aluminum particles on the surface so often reflects the binder distribution in the underlying propellant matrix (Fig. 12). However, this pattern is locally transitory as the burning front progresses through the matrix (Fig. 16), and we are concerned with the corresponding transitory nature of the environment of any aluminum particle or accumulate. The detail in Fig. 16 suggests how the environment of the accumulating aluminum gradually changes at a given location, until the accumulate is substantially surrounded by oxidizer products, and possibly by tips of the binder-oxidizer diffusion flame canopy. At this time, the underlying "sticky" binder melt is presumably gone, and one might expect the accumulate to be only tenuously held to the burning surface, and ready to ignite or leave the surface.

It is the foregoing reasoning that led to the "pocket" model of

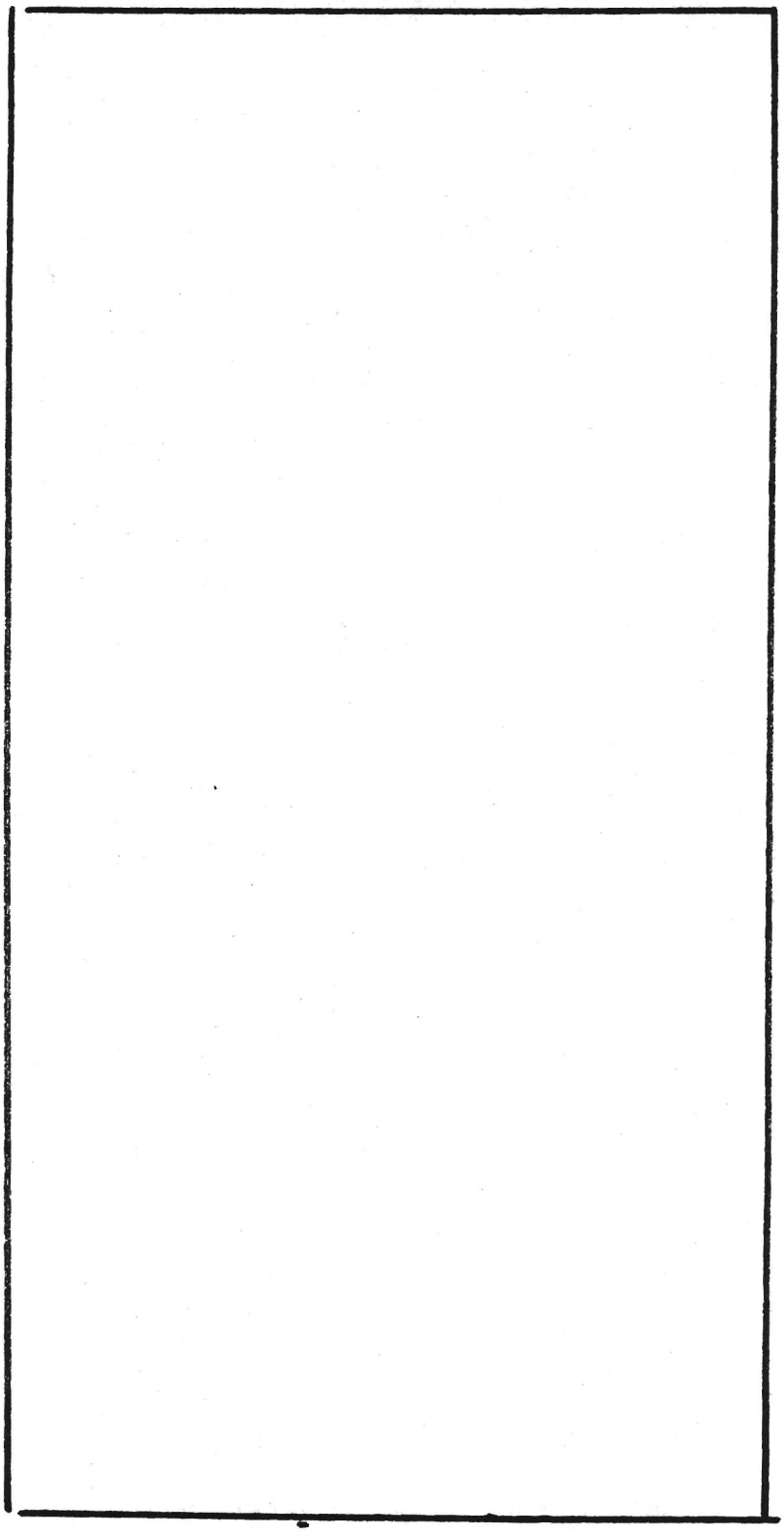
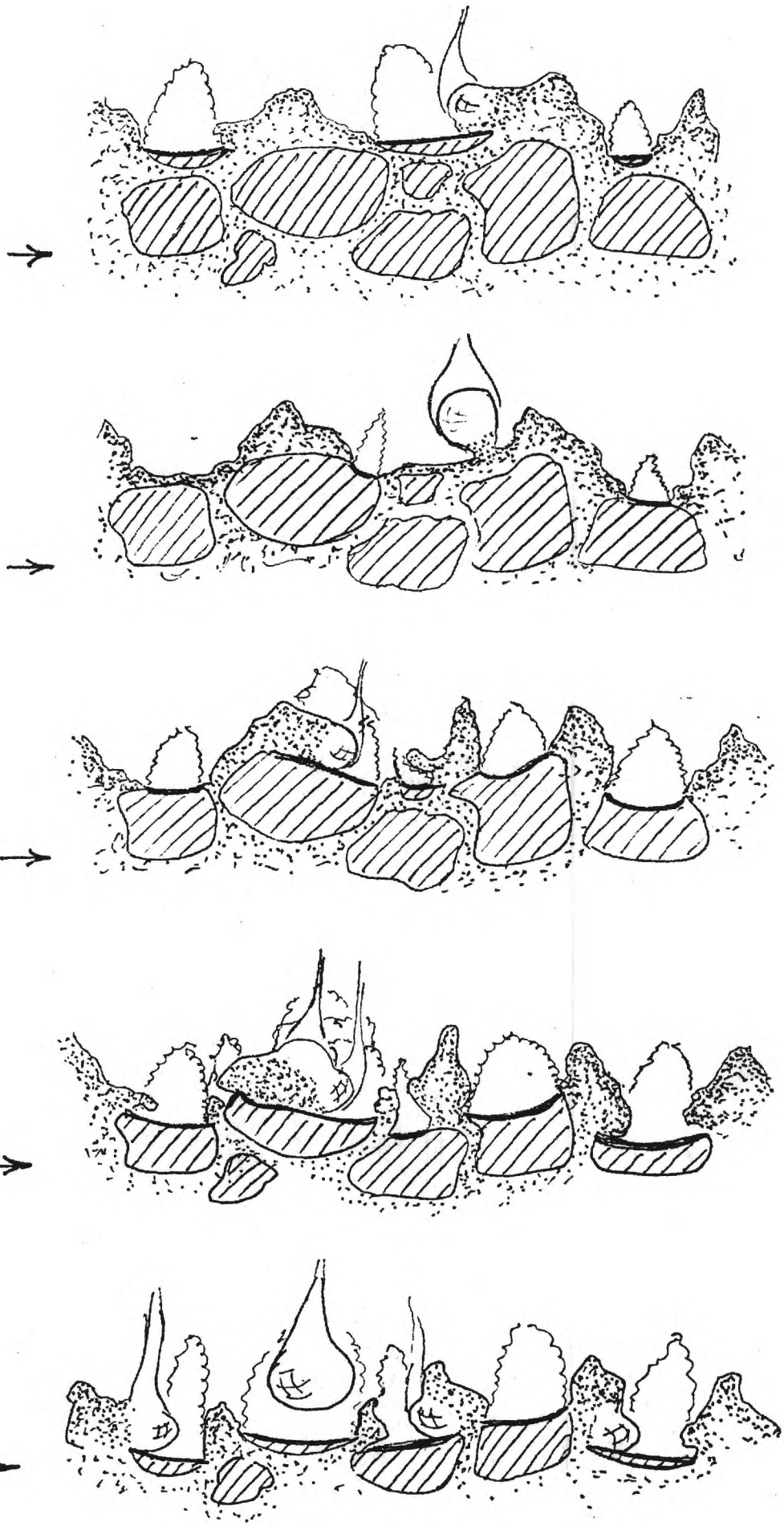


Fig. 16 Sketch depicting the concentration of aluminum in the binder areas of the burning surface, and subsequent exposure of underlying oxidizer particles.



accumulation-agglomeration (R-34), which rests on the fact that there are concentrations of aluminum particles in the propellant microstructure located at those sites of larger binder content among adjoining AP particles. The model hypothesizes that the aluminum particles in these "pockets" of binder accumulate only until the binder in the pocket is pyrolyzed and underlying AP exposed, at which time the accumulated aluminum detaches and melts into an agglomerate. This relates the final aluminum agglomerate size to the amount of aluminum in the binder pocket, and the agglomerate size is correspondingly dependent on the aluminum concentrations in the propellant microstructure and is sensitive to oxidizer particle size, but insensitive to aluminum particle size (R-34). Observed correlations have supported these hypotheses under favorable combustion conditions (R-35). However more extensive accumulation occurs at low pressures and with very high aluminum concentrations (i.e., pocket accumulates are interconnected). Further, accumulates form also with propellant microstructures having no conspicuous binder pockets (e.g., propellants using multimodal AP particle size distribution), indicating that the "pocket model" is not sufficient as a scheme for explaining agglomerate size. Thus existing information offers qualitative insight into accumulation behavior, but more understanding of the detailed mechanisms is evidently needed to really understand formation of these more complex accumulates. In order to extend the picture of accumulation beyond the simple pocket model, a more basic look will be made in the following at the information bearing on accumulate formation.

5.3 How Accumulates Form

5.3.1 Adhesion - Cohesion

In the last Section it was hypothesized that aluminum accumulation was a result of adhesive action by melts of binder and/or binder decomposition intermediates (a subject discussed in Section 4.1). While very little is actually known about the microscopic and chemical details in the combustion zone, the hypothesis of adhesive action is given credence by a number of unambiguous observations.

a) The aluminum does accumulate and adhere to the surface, and particles do adhere to each other.

b) "Melting" and charring of binders is observed in hot stage microscope tests, (R-36).

c) Liquid layers are observed on binder surfaces during combustion of unaluminized propellants and sandwiches (R-37).

d) Accumulate removed from the burning surface after quenching has been shown to include materials of lower density than aluminum, probably carbonaceous (R-38).

e) The formation of accumulates is affected by the type of binders involved (R-39).

Thus it seems very likely that the initial formation of accumulates results from adhesion due to binder intermediates. As will be seen below, this is not the only means of formation that must be considered.

During the life history of an accumulate, it proceeds to a progressively hotter region of the combustion zone. The initial formation of accumulates by adhesion occurs as a natural consequence of concen-

tration in a layer of molten binder, primarily at temperatures below or near the melting point of aluminum, and in a fuel-rich atmosphere. In the course of its stay on the burning surface, the accumulate apparently reaches temperatures considerably higher than the melting point of aluminum. (This view was discussed in Section 4.2 and will be discussed in Section 6, but can be inferred by the fact that aluminum survives for some time on the surface, exposed to heat flux from the diffusion flame.) Laboratory tests on binders and aluminum (R-40) indicate that the binders decompose rapidly at 500-700°C, and that aluminum powders are active in that range. Some particles will no doubt be released from the surface (Fig. 15, 16) due to reduced adhesive action by the decomposing binder. On the other hand, many, or most particles will (depending on the binder) adhere directly to each other due to direct particle interaction, especially if the binder adhesive action survives to the melting point of the aluminum where the activity of the aluminum increases (R-41). Once aluminum particles become stuck together by their own interaction, they are resistant to ignition because of the oxide film on all surfaces. However, the transition from an accumulate produced by binder adhesive action to an accumulate preserved by direct particle interaction ("cohesion" or "sintering"), is a delicate one in which both binder and aluminum powder characteristics are believed to be critical to the integrity of the accumulate. However, the interplay of binder adhesion and direct Al particle cohesion, in combustion zone environments is not far beyond a speculative state of knowledge to date.

5.3.2 Heating Tests on Aluminum Powder

Because of the difficulty in observing the formation of accumulates in the combustion zone, the process has been studied in a variety of more simple laboratory tests, the simplest being controlled heating of

aluminum powders in controlled atmospheres. The electrical conductivity tests noted in Section 2.3 are an example, but the most extensively used technique is the hot stage microscope (HSM) (R-42). It was observed early in such studies that:

a) Particles expanded visibly at the melting point (R-43).

b) Contacting particles often coalesced (inert atmosphere) in the temperature range 700 - 900°C, leaving visible fragments or intact empty oxide shells near the agglomerate (Fig. 17, R-44).

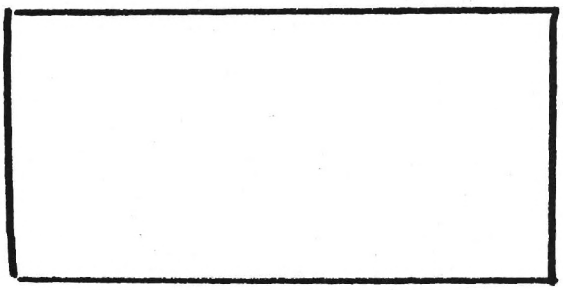
c) Particles on platinum surfaces "drained" leaving empty oxide shells (Fig. 18, R-45) in various states of collapse.

d) In b, when the atmosphere that was used was oxidizing (air or O_2/N_2 mixtures), coalescence of particles was impeded, and instead oxide-coated bridges formed between particles (Fig. 19, R-46).

e) Enhancing the initial oxide coating on the particles by baking the powder in an oxygen atmosphere not only raised the temperature at which a drop in electrical resistance of powders occurred (Fig. 5), but also reduced the tendency of particles to coalesce, drain or bridge together in the hot stage microscope tests (R-47).

The mechanistic basis of the observed behavior in the HSM was suggested by earlier hot plate drop (HPD) tests, in which aluminum particles were dropped on a sapphire plate preheated to 1400°C by a burner flame (R-48). These particles were examined later with a scanning electron microscope (SEM), and showed particles in various stages of coalescence (Fig. 20). Detailed examination showed

a) that the oxide coating had been extensively cracked, presumably



.Fig. 17. Behavior of aluminum powder heated to the 700 - 900°C range in argon. Note agglomeration and drainage of oxide shells. Pictures taken after cooling.

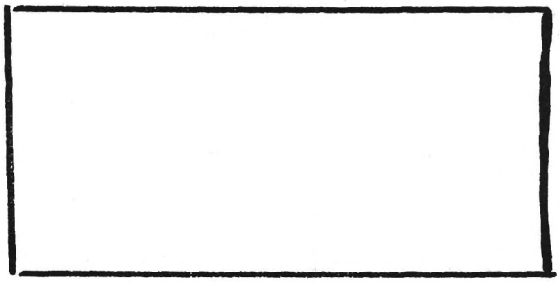


Fig. 18 Aluminum particles heated on platinum wire. Surface tension causes characteristic cone, leaving emptied collapsed oxide shell. Picture taken after cooling, SEM.

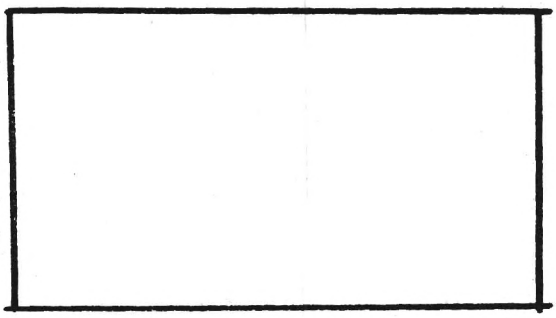


Fig. 19 Behavior of aluminum powder heated to the 700 - 900°C range in air. Note absence of agglomeration, occurrence of sintering between particles. Picture taken after cooling.

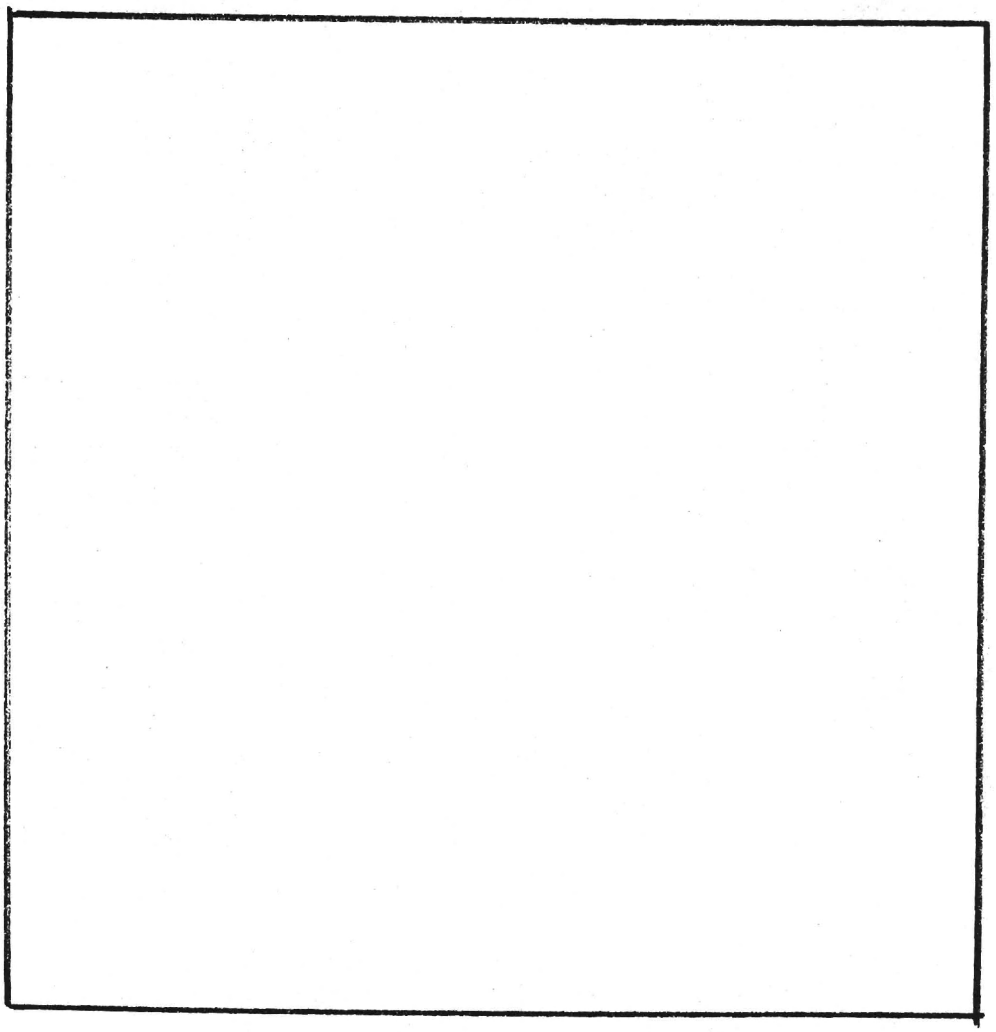


Fig. 20 Behavior of special spherical aluminum powder when dropped on a flame-heated plate at 1400°C. Note large agglomerate, crack patterns on oxide surfaces, wrinkling during cooling. SEM.

due to differential thermal expansion of the metal and its oxide coating,

b) that aluminum leaked through the cracks, leading to agglomerates and to empty oxide shells (Fig. 21),

c) that some contacting particles were sintered together (Fig. 22, 23) without draining,

d) that aluminum leaking through cracks at free surfaces tended to oxidize in place, forming beaded ridges (Fig. 23).

The aluminum particles leading to the above observations by SEM were rather unique particles, in that they were spherical; relatively large; and appeared to have very thin, uniform oxide coating (R-49). Similar hot plate drop tests have been made on an electrically heated plate (R-50) using propellant grade aluminum similar to that in the HSM and electrical resistance tests. These tests do not reveal well-defined cracks in the oxide shell, although drainage, agglomeration and bridging do occur in varying degree (depending on atmosphere, aluminum powder, proximity of particles, and temperature). Some particles show a unique form of response (Fig. 24a) (R-51) suggestive of inflation during heating, followed by collapse during cooling. It is also noted in HSM tests that particles often exude aluminum into wart-like protrusions during heating, often with indication of subsequent collapse of the oxide shell during cooling (Fig. 24b) (R-51).

Collectively, the heating tests on aluminum particles and powders (electrical resistivity, HSM, and HPD + SEM tests) demonstrate that above the aluminum melting point, the aluminum is no longer fully and

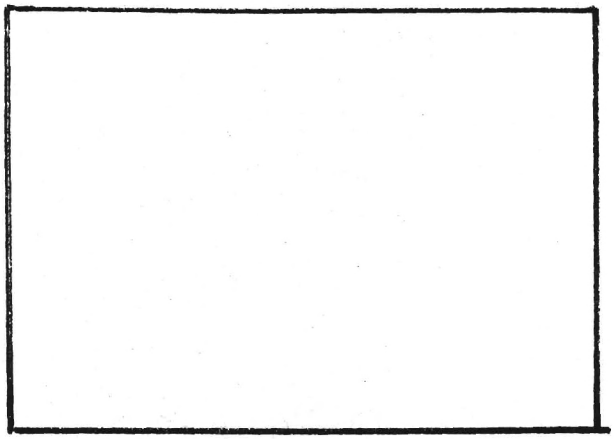
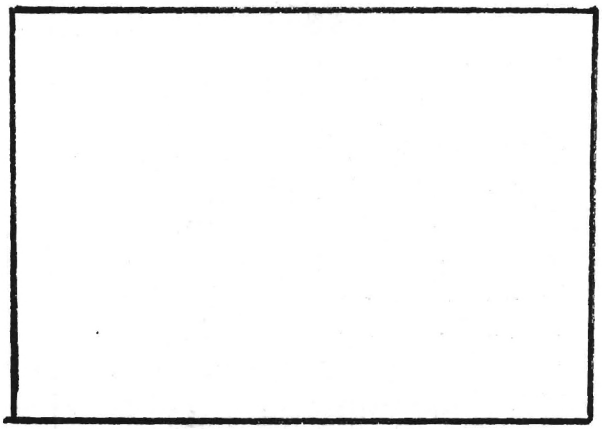


Fig. 21 Drained, cracked oxide shell from same test as Fig. 20.

Fig. 22 Sintering of contacting particles; same test as 20, 21. See also Fig. 23.



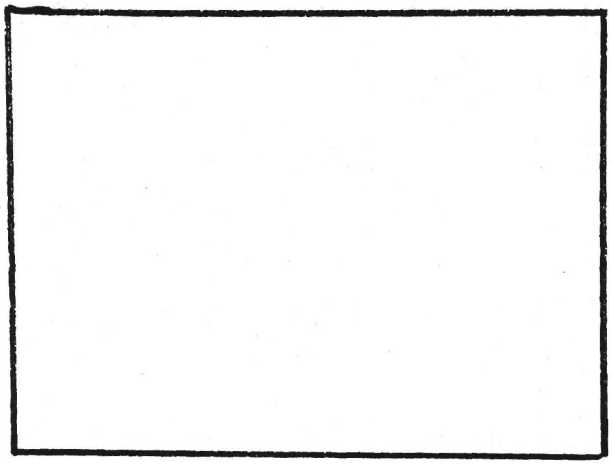


Fig. 23 Sintering, and beaded ridges sealing cracks; same test as Fig. 20 - 22.

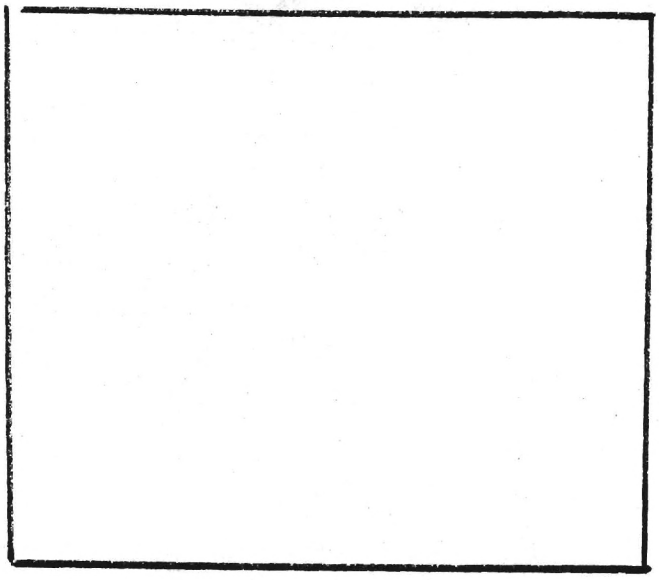


Fig. 24a Collapse of oxide coating due to aluminum contraction during cooling.

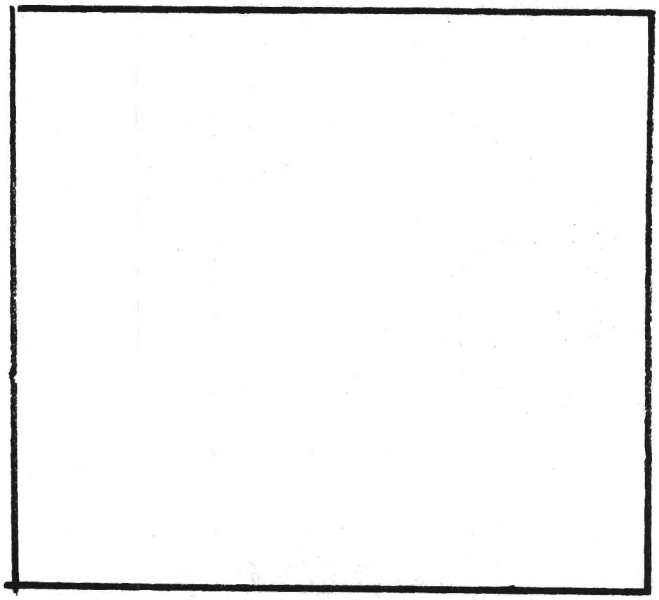


Fig. 24b Evidence of extrusion of aluminum during heating (to form the wart-like protrusion), followed by collapse of the oxide coating of the partially drained particle during cooling.

Fig. 24 Behavior of propellant-grade aluminum particles; samples heated to 900°C in an oxidizing atmosphere.

consistently contained in oxide shells. In inert atmospheres the aluminum can drain completely from the shell, and adjoining particles can agglomerate if contact is made, leaving empty oxide shells. In oxidizing atmospheres, the "escaping"aluminum is oxidized quickly, and thus does not drain so readily from the oxide shell. However, contacting particles sinter together, presumably by oxidation of escaping aluminum at points of contact among particles.

5.3.4 Accumulates in Simple Combustion Systems

To this point it is easy to believe that aluminum in a propellant can concentrate, form accumulates, and adhere to a binder surface. It is less clear how to tell in advance that surface accumulates will linger on the surface and sinter as the binder adhesive pyrolizes (although it seems clear that such processes do occur). Some insight on this issue is provided by observations of combustion of aluminum in "model propellants." Two examples are the combustion of samples made by a) pressing AP/Al powder mixtures, and b) laminating aluminized binder between two sheets of AP (sandwiches).

Combustion of dry-pressed powder mixes (R-52) has shown that aluminum accumulates on the burning surface even in the absence of binder adhesive action. In other words, the environment at the burning surface of the AP is not necessarily conducive to either ignition or detachment of the aluminum. In addition, some form of sintering occurs. The practical significance of this is that in propellant combustion the different chemical environment does not prevent the accumulation-cohesion from occurring in the manner observed in controlled heating

tests. That is, the exposure of accumulating aluminum to underlying oxidizer during regression of the propellant burning surface is not necessarily the terminal phase of accumulate growth as assumed in the pocket model. Instead, interaction with the diffusion flame may be important in limiting the growth of accumulates, and the proximity (and temperature) of that flame may be an important factor in accumulate size. It is also of interest that the accumulation-shedding of aluminum on the burning surface of dry-pressed AP-Al pellets is often periodic in manner (Fig. 25, 26) (R-53,54), suggesting that the departure from the surface is a result of growing resistance to flow of gases from the underlying AP.

The nature of accumulate formation in the propellant combustion zone is also suggested by sandwich-burning experiments involving aluminized binder (R-55). In these tests, behavior of accumulates is observed by combustion photography. The accumulates form in the exposed surface of the binder layer (Fig. 27). Their subsequent behavior can be classified in three categories, related to where they are located relative to the oxidizer-binder interfaces. Accumulates formed in the binder at locations most remote from the interfaces leave the surface as accumulates, while those near the interface (and diffusion flame) tend to coalesce and burn when they leave the surface. Some accumulates "flop" over onto the burning AP surface, and are observed to adhere without coalescence for some time. These observations reinforce the views that

a. Accumulates are formed initially by adhesive action of the binder.

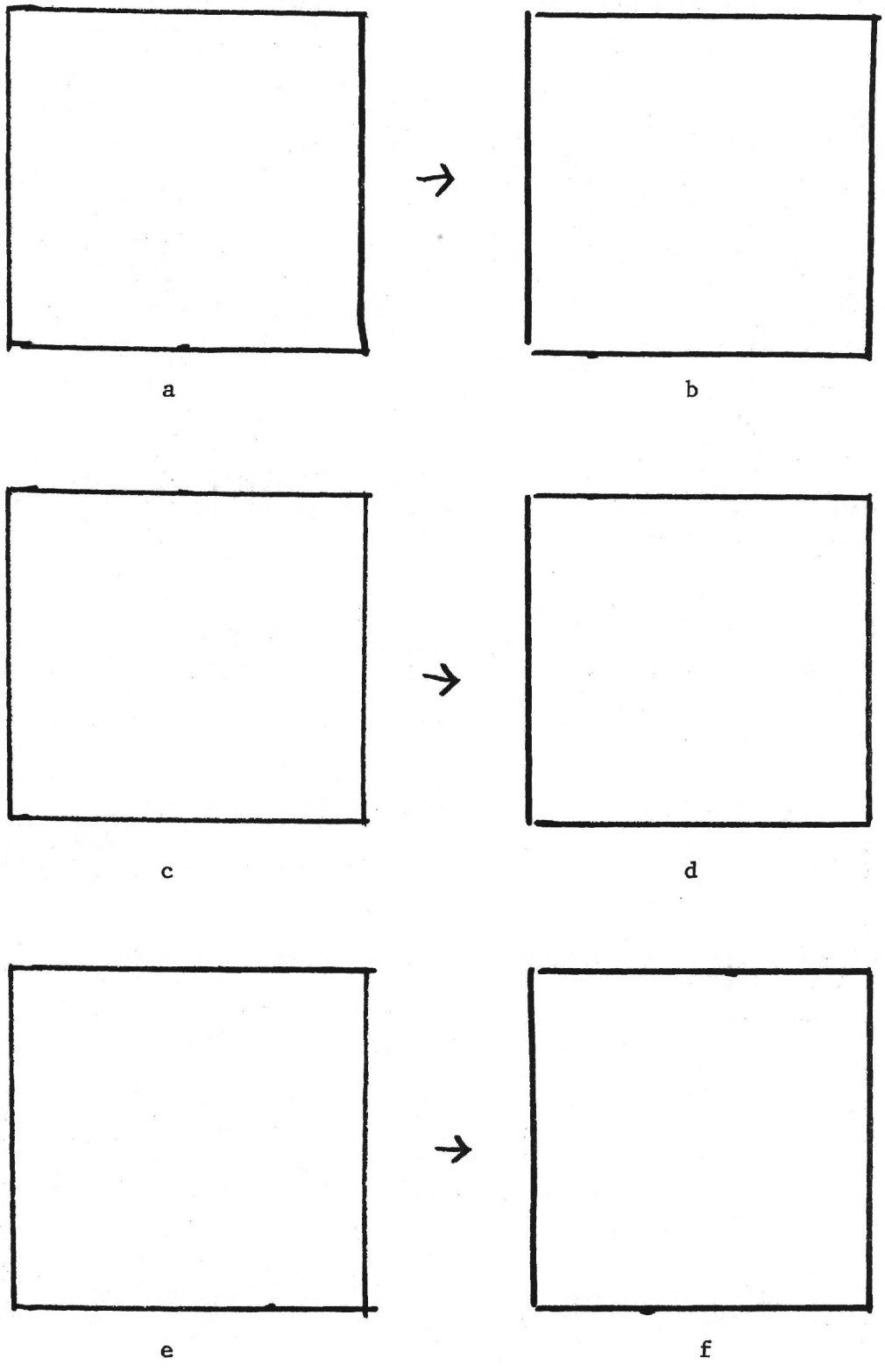


Fig. 25 Inflammation and detachment of accumulated aluminum from the burning surface of a dry-pressed sample of AP-Al mixture (R-53). (Made from 16mm motion pictures at frames per second.)

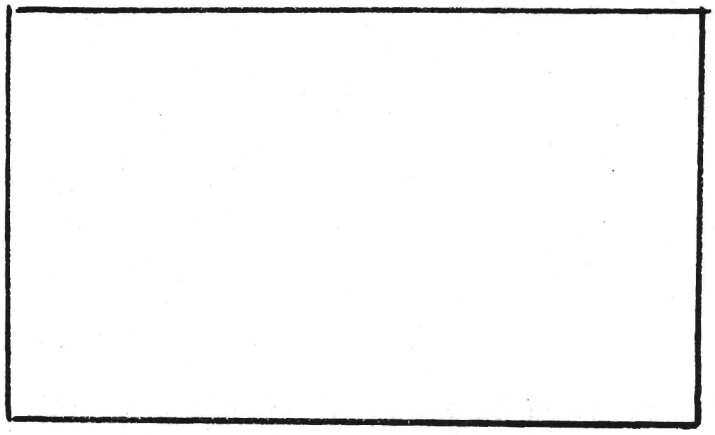


Fig. 26 Periodic luminosity from combustion of sample of dry-pressed AP-al reflecting powder accumulation-detachment-combustion of aluminum (R-54).

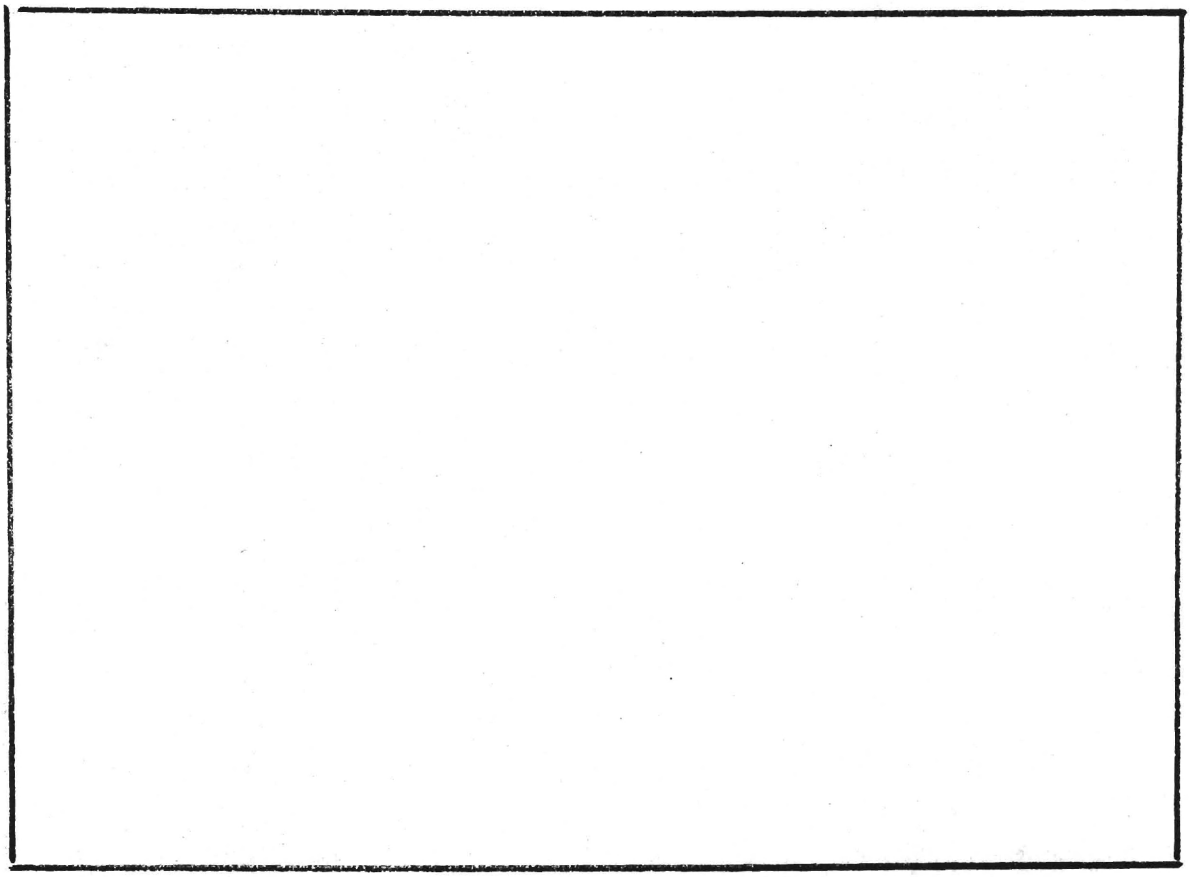
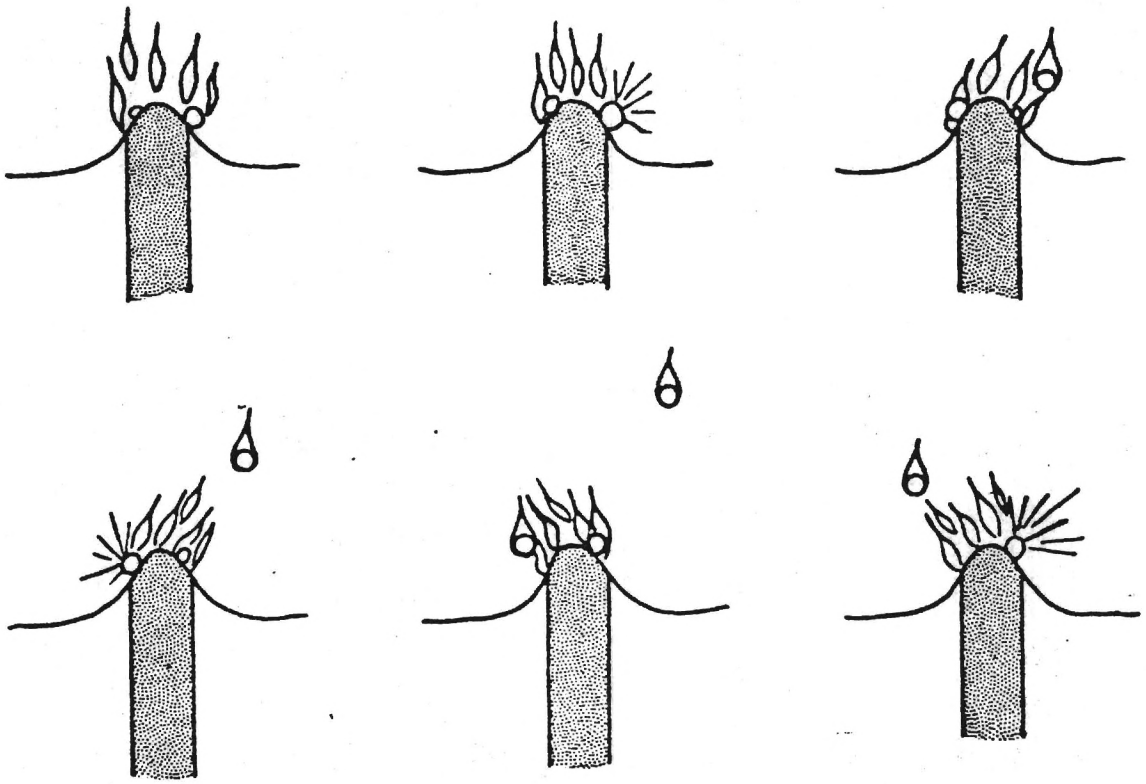


Fig. 27 Sketch showing sequential appearance of aluminum accumulation during burning of AP-binder "sandwiches" with aluminum in the binder (from 16mm movies).

Fig 27



b. Ignition of accumulates is impeded by persistence of a fuel atmosphere.

c. Accumulates can survive and adhere to the oxidizer burning surface, even accumulates formed on the binder surface

d. The diffusion flame quickly breaks down the structure of detached accumulates.

Collectively, the results in this section (5.3) concerning the behavior of aluminum in controlled environments and in simple combustion systems are consistent with interpretation of propellant combustion behavior described in Section 5.2.

a. The behavior of the binders during heating is indeed favorable for concentration and adhesion of aluminum particles without ignition.

b. It is plausible that aluminum particles may coalesce to form agglomerates while still in a binder (fuel) environment (on the pyrolizing binder surface, before all binder is gone from the particles).

c. It is plausible that the accumulated particles may survive in an interconnected state (accumulates) when exposed to the AP oxidizing environment, without immediate agglomeration or ignition. Under these conditions the binder residues are probably consumed and particle cohesion occurs through sintering.

d. The behavior in b and c can occur on the burning surface at temperatures about the aluminum melting point.

e. Ignition of accumulates does not occur readily in the AP deflagration zone, and consequently is dependent on exposure to the diffusion flame. Accordingly, conditions conducive to surface proximity of the diffusion flame to the accumulate (or the release of the accumulate into the flame) are conducive to agglomeration-ignition, which is the termination of accumulate growth.

5.4 Variety of Accumulates

From the arguments regarding the nature of the combustion zone and how accumulates form, one might anticipate that the wide variation in propellants in use would lead to a variety of accumulation "habits". Indeed the variety is so great that detailed discussion is relegated to a later report. In the present Section a description of most typical behavior and trends is presented.

5.4.1 Smooth Accumulate Layers

Ammonium perchlorate - hydrocarbon rubber - aluminum propellants usually have an irregular grey layer of aluminum on the burning surface, the irregularity being related to coarseness of the AP and to combustion zone factors affecting ignition of the aluminum. A smooth layer (Fig. 28) is favored by fine AP, medium aluminum concentration (10 - 20%), intermediate pressure (200 - 600 psia), Al particle size smaller than AP particle size, and fairly high solids loading. This type of accumulate layer apparently evolves from conditions where favored accumulation sites (pockets) are absent, aluminum is relatively homogeneously distributed in the propellant, regions of molten binder are closely spaced on the

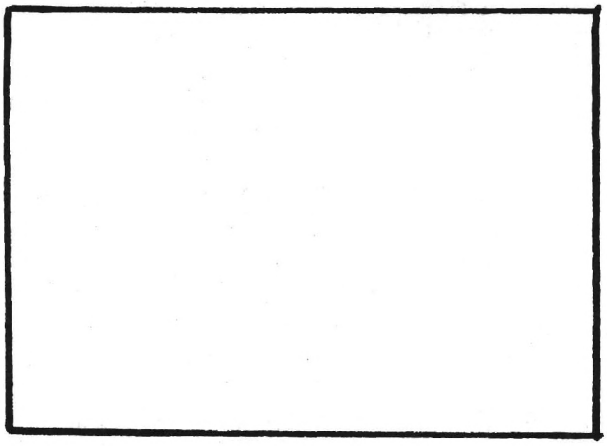


Fig. 28 Smooth aluminum accumulate layer typical of propellant with fine oxidizer particle size: frame from motion picture.

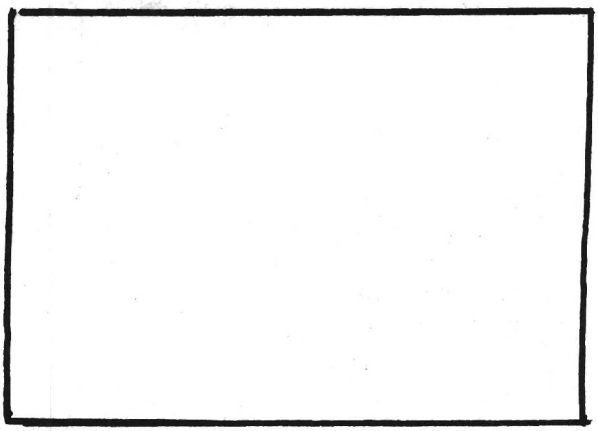


Fig. 29 Irregular aluminum accumulate layer typical of a propellant with coarse AP, low AP content, high al content, or low pressure.

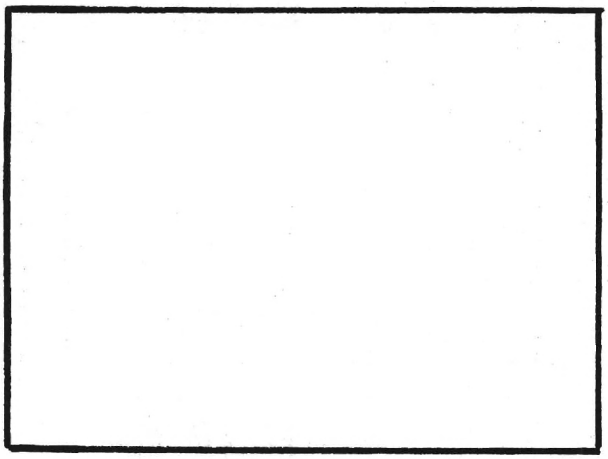


Fig. 30 Accumulate filigree resulting from extreme conditions of Fig. 29, specifically, high Al content. Also typical of NC-NG-AP-HMX-Al propellant with low AP content or low pressure.

surface beneath the accumulating aluminum, conditions are favorable for extensive surface-wise sintering, and ignition conditions for the aluminum are good enough to prevent large accumulates from protruding or flapping far from the propellant surface. The accumulation layer usually breaks down either by cracking to form "flake accumulates" (low pressure), or by emitting smaller, already igniting fragments. These will be described further in Section 6.

5.4.2. Irregular Accumulate Layer

An irregular layer of aluminum occurs (Fig. 29) when the oxidizer is coarse, the pressure low, the Al concentration high, or the oxidizer concentration low. These conditions correspond to initially irregular distribution of aluminum in the propellant (in binder pockets) and unfavorable conditions for ignition or removal from the surface (permitting interconnectedness among pocket accumulates). The accumulate layer breaks down locally by either local ignition or gas flow forces, causing partial break-away of parts of the layer to give large surface-attached accumulates. When aluminum concentration is exceptionally high, these lingering accumulates may be interconnected, to give a filigree-like accumulate hundreds of micrometers across loosely connected to the propellant surface (Fig. 30).

5.4.3 Most Typical Accumulate Layer

The <u>most typical</u> aluminum accumulation on the burning surface appears as an irregular grey layer from which individual accumulates emerge abruptly without visible interaction with neighboring parts of the layer. The size of the accumulates is extremely varied, with the largest being of the same order as the "pockets" among the coarser AP particles ($\sim 10^3$ aluminum particles). As will be noted later, the emergence of recognizable individual

accumulates from the surface is often concurrent with their ignition. It is probably significant that the "most typical" propellants have blends of different oxidizer sizes, and that the corresponding "most typical" accumulates are often of sizes large enough so that they overlay the fine oxidizer and appear to be size-limited by the coarse oxidizer. The actual details of processes determining accumulate size for these high-solids propellants are only partially understood because of the complexity of the microstructure, but some significant studies based on systematic variation of particle sizes of ingredients are in progress or recently completed (R-56). In addition, some speculative interpretation is made in Section 6.

5.4.4 Other Distinctive Accumulate Behavior

It is sometimes observed that ignition of aluminum will occur in an accumulate layer like that in 5.4.3, without prior evolution of any identifiable accumulate in the layer (Fig. 31). In such situations the concept of an accumulate may seem superfluous, since no definite accumulates are seen in the aluminum layer. However, inability to observe does not prove nonexistence, and the fact is that a specific part of the layer is involved in each surface ignition event, a part relatable to the propellant microstructure. Indeed it is observed that in certain propellants the ignited agglomerate (See Section 6.4) will linger on the surface for some time without appreciable movement or involvement of neighboring parts of the aluminum layer.

Another class of aluminum behavior is that observed when coarse aluminum powder is used, so that AP and Al particles are of comparable size. In this case, the aluminum particles are mostly surrounded by the more numerous AP particles. Then the Al particles each have their own Al particles and AP-binder diffusion flame canopy. Thus they tend to leave

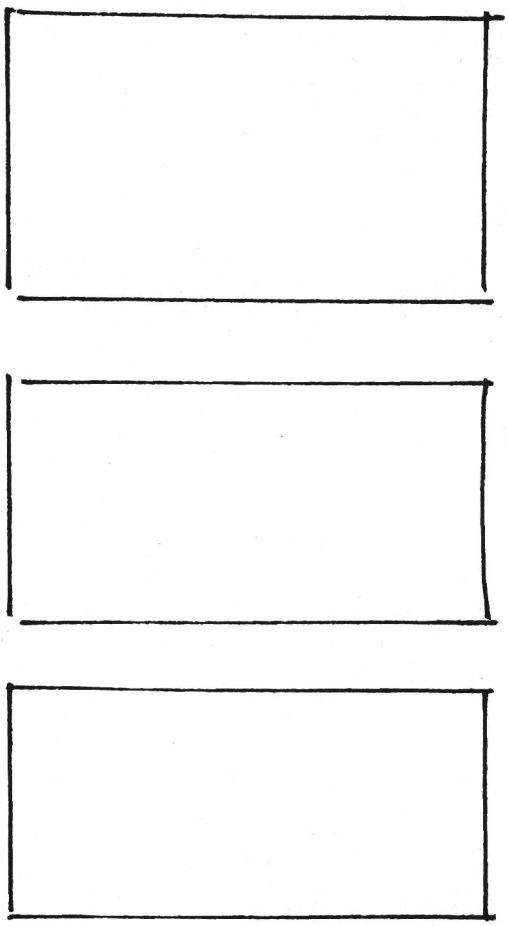


Fig. 31 Ignition in an accumulate layer without prior identifiability of an associated accumulate.

Fig. 31 -- Needs a 3-frame sequence showing

1. Smooth surface
2. Igniting agglom. in surface
3. Burning agglom. just above the surface.

These should be in very close time sequence to illustrate th point in question. "bursting from surface" ANB 3066

Fig. 31. Legend: "Ignition in an accumulate layer without prior identifiability of an associated accumulate."

Sequence of three frames showing emergence of burning accumulate - agglomerate in second frame, first frame 2 or 3 frames earlier with no definable accumulate. ANB 3066 propellant pictures should provide example from Code 388 library.

the surface before they encounter other aluminum particles, and only minimal accumulate formation occurs unless the aluminum content is unusually high.

In still another class of aluminum behavior on the burning surface, the aluminum layer melts down and burns extensively on the propellant surface (Fig. 32), without identifiability of specific accumulates in the process. Such behavior is observed with propellants using thermally stable binders; in spin stabilized motors where the "free" aluminum droplets are centrifuged towards the burning surface; and with propellant compositions that provide poor oxidizing atmosphere for aluminum and high retention by surface melt (e.g., compositions with HMX instead of AP).

5.4.5. Double Base Binder

While peripheral to the scope of this report, some mention of accumulate behavior in propellants with double base binders is useful to clarify often conflicting views on aluminum behavior. Attention will be directed to simple aluminized double base propellants, and composite propellants with double base binders. Experience with the latter involves primarily formulations (Fig. 6c) with granular HMX as an ingredient and with low AP concentration. In the case of double base propellants, the surface accumulation of aluminum presents less in the way of structural features, as one would expect of a homogeneous matrix. However, some reports (R-57) cite accretion of aluminum on carbon shreds that are normally present in the surface, while other reports (R-58) describe accretion as a result of burning agglomerates rolling around the surface. Actually, very little combustion photography has been done with the external illumination needed to see surface behavior of nonluminous material, so the primary

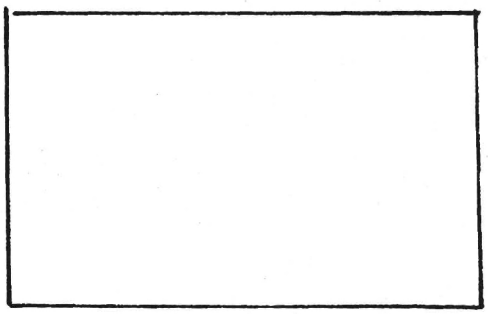


Fig. 32 Aluminum persistence on the surface even after ignition - puddling. Accumulates evolve without individual surface identity.

point to be made here is that one should not presume the behavior of aluminum in such propellants will be the same as in AP/HC/Al propellants.

With composite double base propellants of the type described above, accumulation behavior covers the range of behavior described above for AP/HC/Al composite propellants. There is a tendency towards a surface-wise connected accumulation of aluminum, with individual accumulates breaking loose from the layer. This layer is smooth when the AP particle size is small, gets very irregular when AP is coarse, AP concentration is low, solids loading is low, aluminum loading is high, or pressure is low. Loosely connected accumulates are more conspicuous than with AP/HC/Al propellants, often constituting a forest of tenuously attached filigrees (Fig. 30, 33) with minimal interconnectedness. High solids or high AP content tend to reduce accumulation.

5.5 Mobility of Surface Aluminum

In the two preceding sections, the mechanistic basis of accumulate formation and the variety of resulting forms were discussed. In general, these processes did not call upon mobility of aluminum particles. Indeed, the dominant role played by adhesive and cohesive processes is inconsistent with the idea of motion of individual particles. If the individual particles were free to move about, they would move away from the surface as individual particles under the influence of the out-flowing pyrolysis products. In any case, the aluminum does eventually leave the surface, and that terminal demonstration of mobility is often preceded by some kind of limited surface-wise mobility. This mobility is of interest for several reasons:

a) Added coalescence of accumulates sometimes occurs due to mobility, affecting accumulate and agglomerate size.

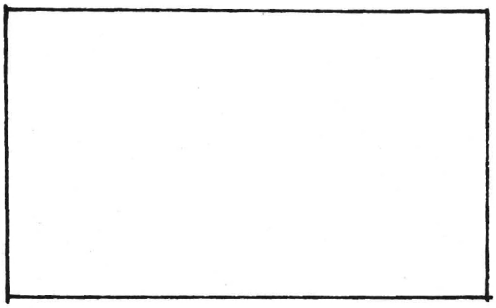


Fig. 33 Oblique view of the burning surface of a CMDB propellant (low AP content), showing "filigree" accumulates loosely attached to the surface.

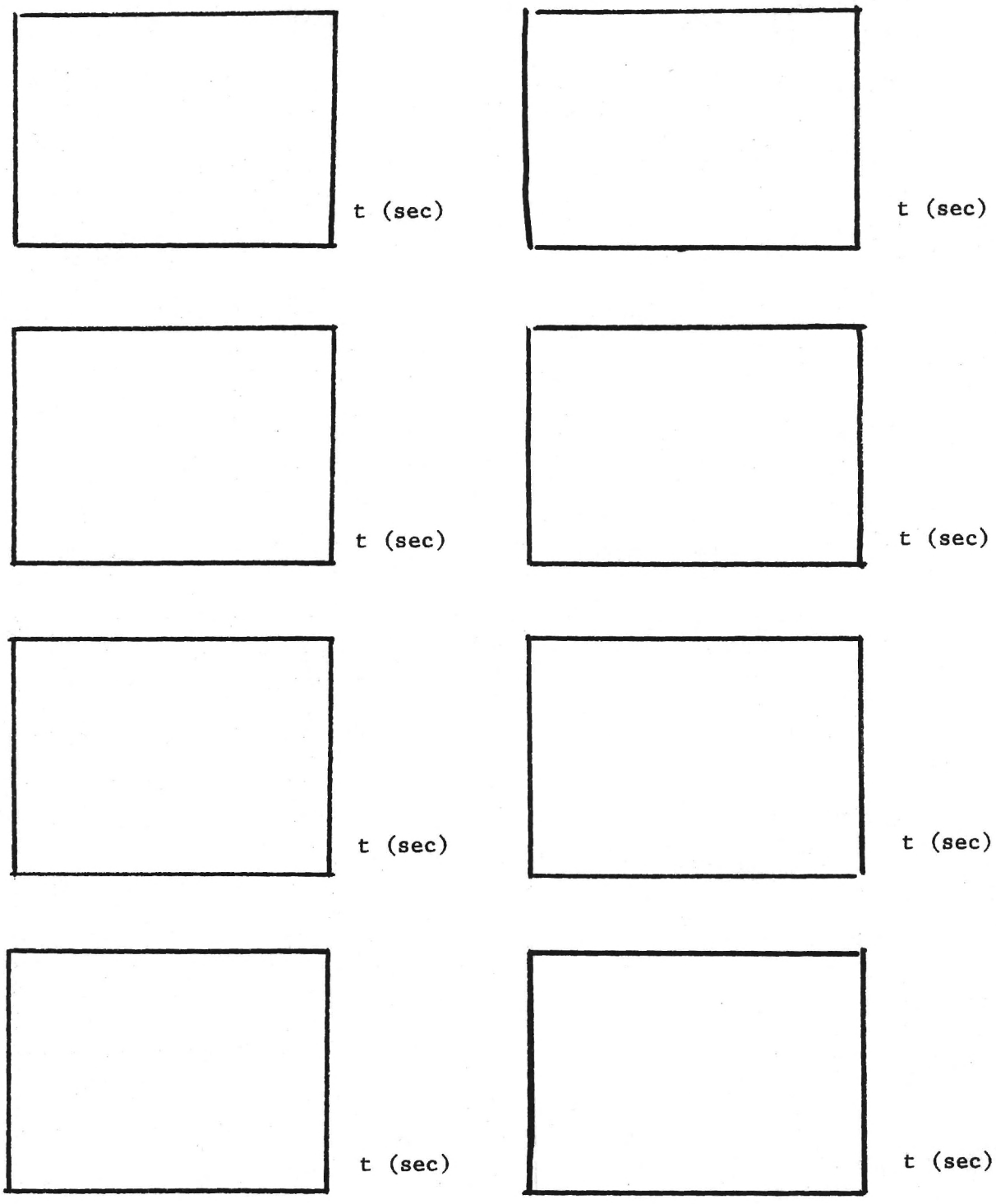
b) Mobility often plays a role in ignition of the accumulate.

c) Mobility is suggestive of vulnerability of the accumulate to surface detachment under the influence of the adjoining gas flow field.

In practice, the details of mobility are closely related to the type of accumulate layer, and will be described in that context, again referring first to propellants with AP - HC binder - Al as the primary ingredients.

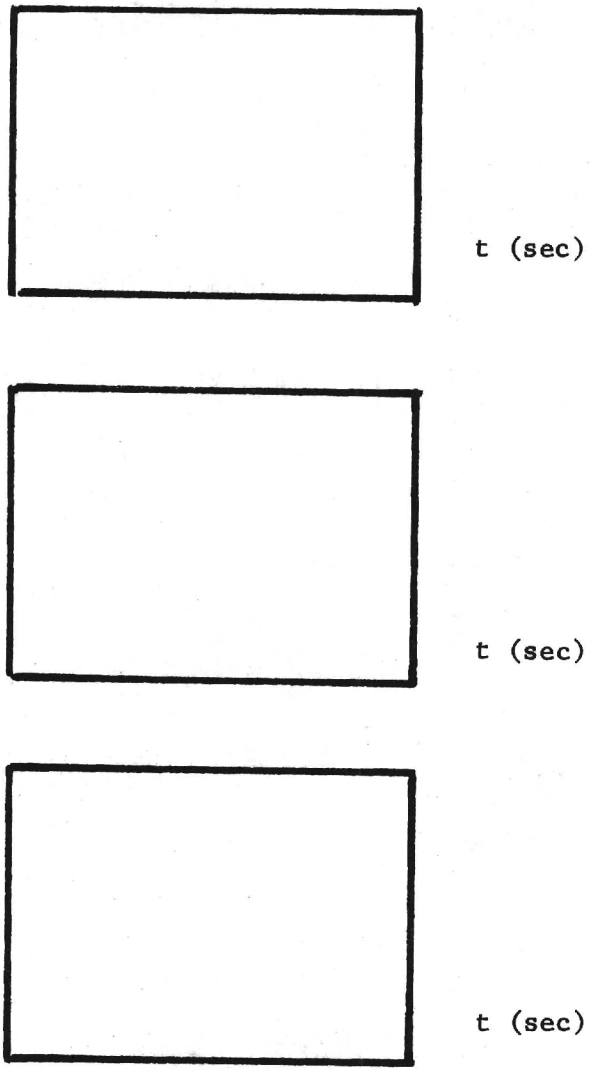
Propellants with smooth layers of accumulated aluminum (Sec. 5.4.1) exhibit cracking of the layer, leading to formation of flakes that break away from the surface. When the burning surface is well illuminated, the flaking is visible in considerable detail at low pressure (< 300 psia). At these pressures there is considerable mobility of the edges of the flake as it is drawn together, but the overall flake remains in place until departure from the surface (Fig. 34a). After the flake leaves the surface, a characteristic time (typically 5 - 100 milliseconds) is required before the layer is ready to shed again. At higher pressure, the size of the flake and time for formation are smaller and details are less visible (Fig. 34b).

Mobility of accumulates has often been reported on the basis of motion pictures without external illumination. The flake formation process is a good example of where movies can be misleading. Thus the coalescence of flakes usually involves a highly visible process of propagative inflamation of the edges of the flakes, which looks like mobility of individual igniting aluminum unless the entire flake is illuminated. This is illustrated in Fig. 35. In reality the mobility in this situation is surface-tension-driven coalescence of the surface-attached flake.



Part a: Low Pressure

Fig. 34 Development of a flake-accumulate.



Part b: High Pressure

Fig. 34 Development of a flake-accumulate.

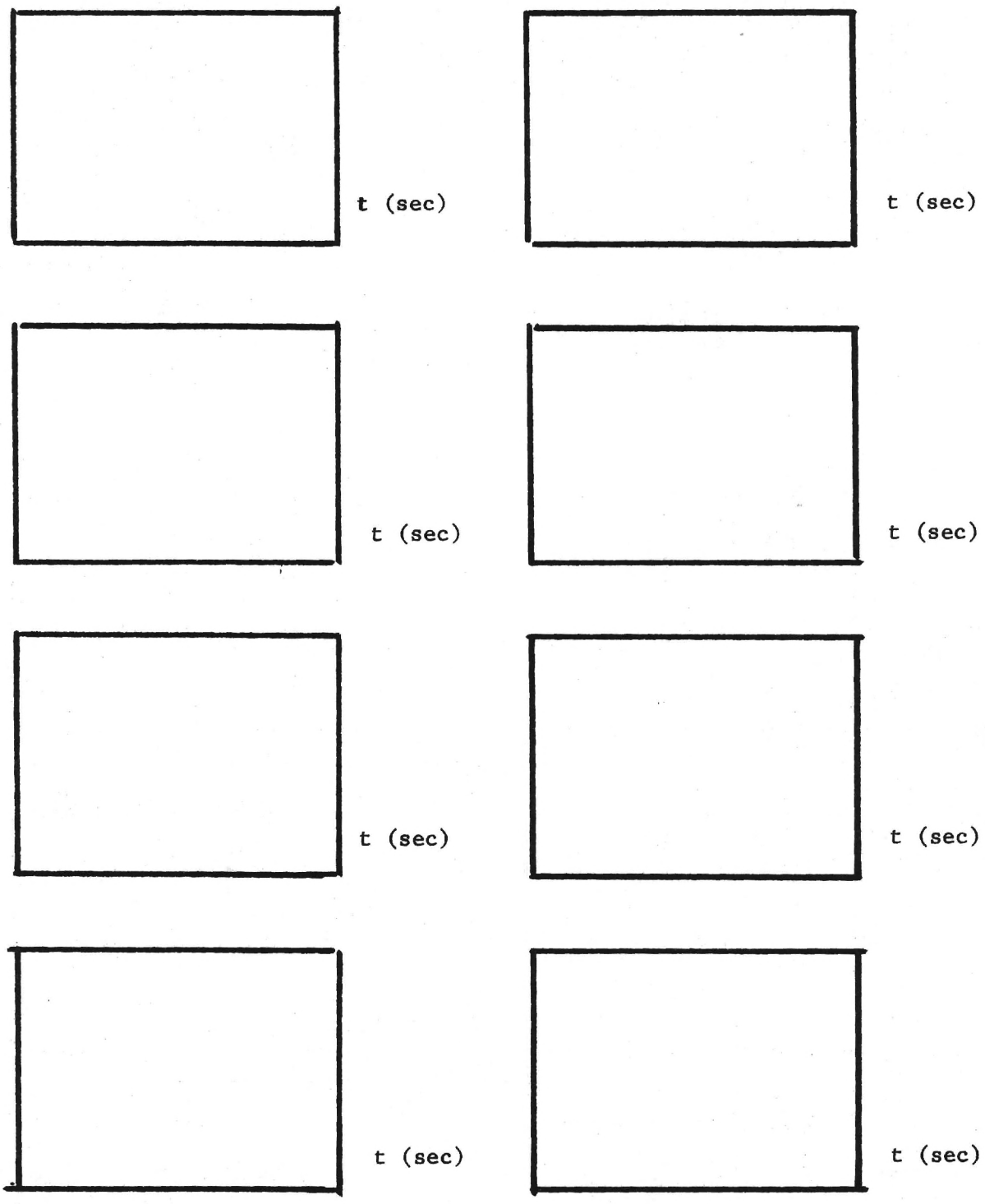


Fig. 35 Appearance of flake-accumulate behavior when seen by self-luminosity: low pressure.

In the case of irregular accumulate layers (Sec. 5.4.2), the irregularities usually reflect nonuniformity in original aluminum distribution in the propellant, associated with the spatial distribution of the larger oxidizer particles. The layer appears to consist of interconnected "pocket" accumulates (Fig. 12). At high pressures these accumulates leave the surface individually. At lower pressures, the accumulates sometimes remain attached to each other, with each detaching in turn from its original surface site and exhibiting appreciable mobility as it awaits detachment of the one or more neighbors to which it is connected. As in Fig. 34a and 35, this mobility may be mistaken for unrestrained mobility if pictures are taken without external illumination. As will be noted later, this illusion is strengthened by the tendency of the first section of accumulate to inflame, making it highly visible compared to the surface-attached accumulates to which it is connected (Fig. 36). When these accumulates are reluctant to inflame, they yield the massive filigree accumulates illustrated in Fig. 30. Hence the filigrees resulting from interaction of accumulates are more common with low pressure, fuel-rich propellant, and coarse AP, where the diffusion flame is more remote, and accumulate ignition is delayed. It is perhaps worthy of repeated note that the population of tenuously held accumulates would be diminished in the presence of the flow environment of a rocket motor, making the subsequent aluminum combustion and Al_2O_3 products sensitive to the flow situation at each location in the motor. Indeed, one might anticipate that the accumulate population would oscillate if the gas flow were oscillatory.

The more typical case of accumulate formation (Sec. 5.4.3) involves relatively little accumulate mobility before leaving the propellant sur-

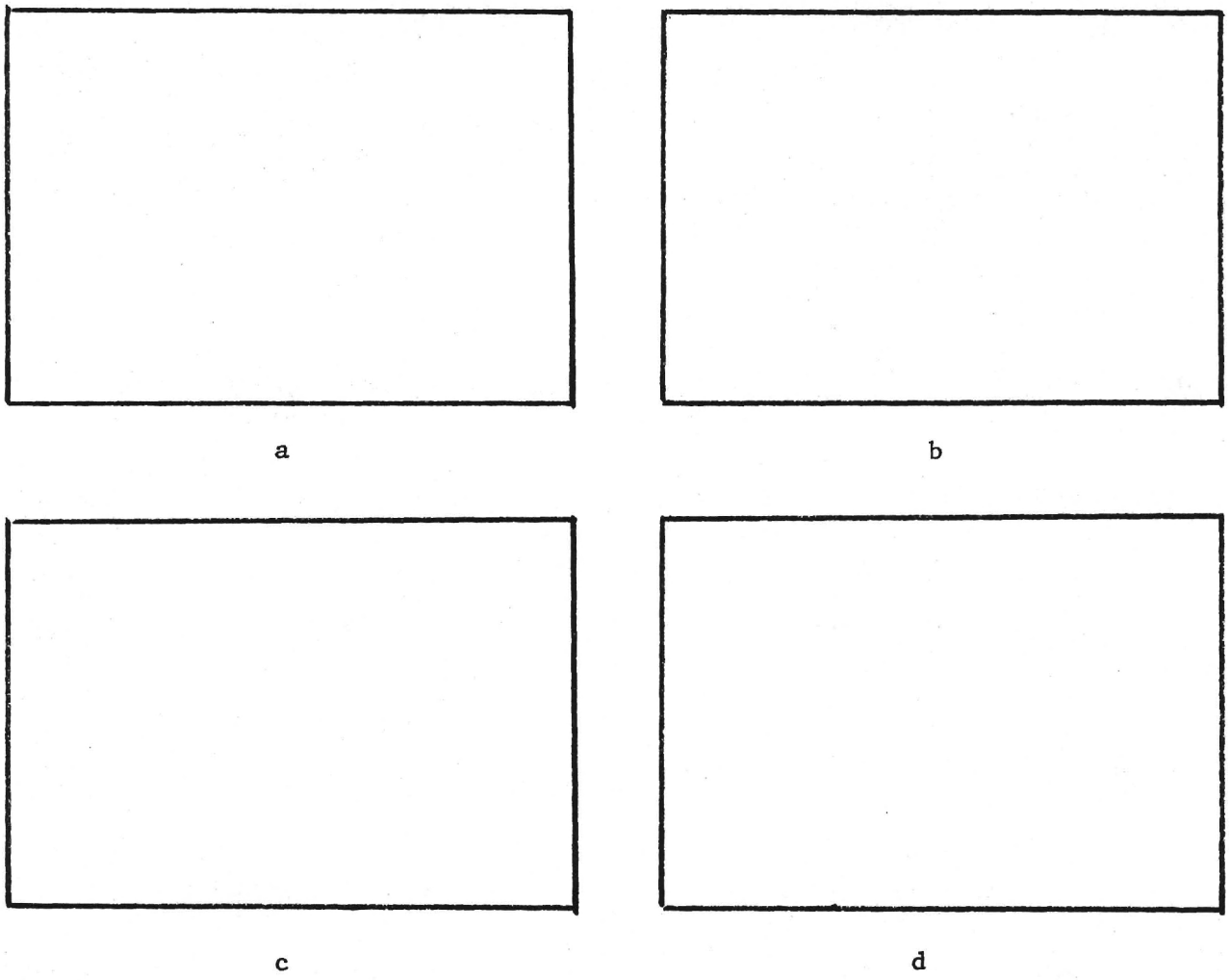


Fig. 36 Detachment of interconnected accumulates.

face, at least on a distance and time scale resolved in combustion photography. Such accumulates usually form in situ, and leave the surface when they first show mobility (Fig. 34b). Under favorable combustion conditions, ignition on the surface will give rise to some brief mobility of accumulates, including mergers with other accumulates (see Sec. 6). During such mobility, the accumulates are ordinarily still attached to the surface, and motion seems to involve response to gas motions or surface tension.

Because of the limited use of aluminized double base propellants in rocket motors, the studies of aluminum behavior in such propellants has been quite limited. Indeed, almost no combustion photography studies have been made using the external illumination needed to show accumulate behavior. Given the homogeneous nature of the propellant, it seems safe to assume that the aluminum accumulates uniformly on the surface; given the stand-off high temperature flame of double base propellants it seems safe that the accumulation will be pressure-dependent. These considerations appear to be a factor in the more well-studied combustion of composite double base propellants described next, and a factor in the aluminum ignition-agglomeration behavior of double base propellants described in Sec. 6. As to mobility, it is often reported[R-58] that burning agglomerates roll around and grow on the surface, a behavior quite rare with AP/HC/Al propellants.

The mobility of accumulates during combustion of composite double base propellants (Sec. 5.4.5) exhibits a range of behavior similar to AP/HC/Al propellants.

The mobility of accumulates during combustion of composite double base propellants (Sec. 5.4.5) exhibits a range of behavior similar to AP/HC/Al propellants, and exhibits trends as functions of AP particle size, AP mass fraction, Al concentration and pressure similar to AP/HC/Al propellants. Experience centers around formulations with relatively low

AP concentration, with substantial HMX (fine), and high binder fraction (Fig. 6c). Such formulations tend to give accumulates that persist on the surface with minimum surface contact giving the appearance of a forest of tenuously attached filigrees (Fig. 33). The issue of flow effects in motor situations merits note here again because of the persistence of tenuously held accumulates seen in the combustion photography (under motor flow conditions such accumulates might be swept away). In one experiment[R-59], the combustion zone was subjected to a suddenly imposed transverse gas flow, which caused the majority of the accumulates to be blown from the surface (Fig. 37), followed by formation of ripples on the surface.

Summarizing mobility effects, they differ conspicuously according to the kind of accumulates, and hence according to propellant and environmental variables. Mobility is generally associated with accumulated aluminum, not original particles, partly because original particles are too small to resolve in the photography. Mobility is important mainly as an indicator of more basic processes such as surface tension, melting formation of individual accumulates from an extensive accumulate layer. Mobility is also suggestive of the vulnerability of the accumulating-"shedding" processes to gas flow conditions in the adjoining channel, including oscillatory gas flow.

5.6 Summary of Accumulate Formation

While the nature of the accumulation-adhesion-cohesion-separation process can be varied in nature, and is no doubt only partially understood, the general nature of the process is established unambiguously. The starting point is the location of the aluminum in the propellant microstructure, immersed in a convoluted, interconnected matrix of binder and protected from oxidizing species. This, in combination with the high boiling point

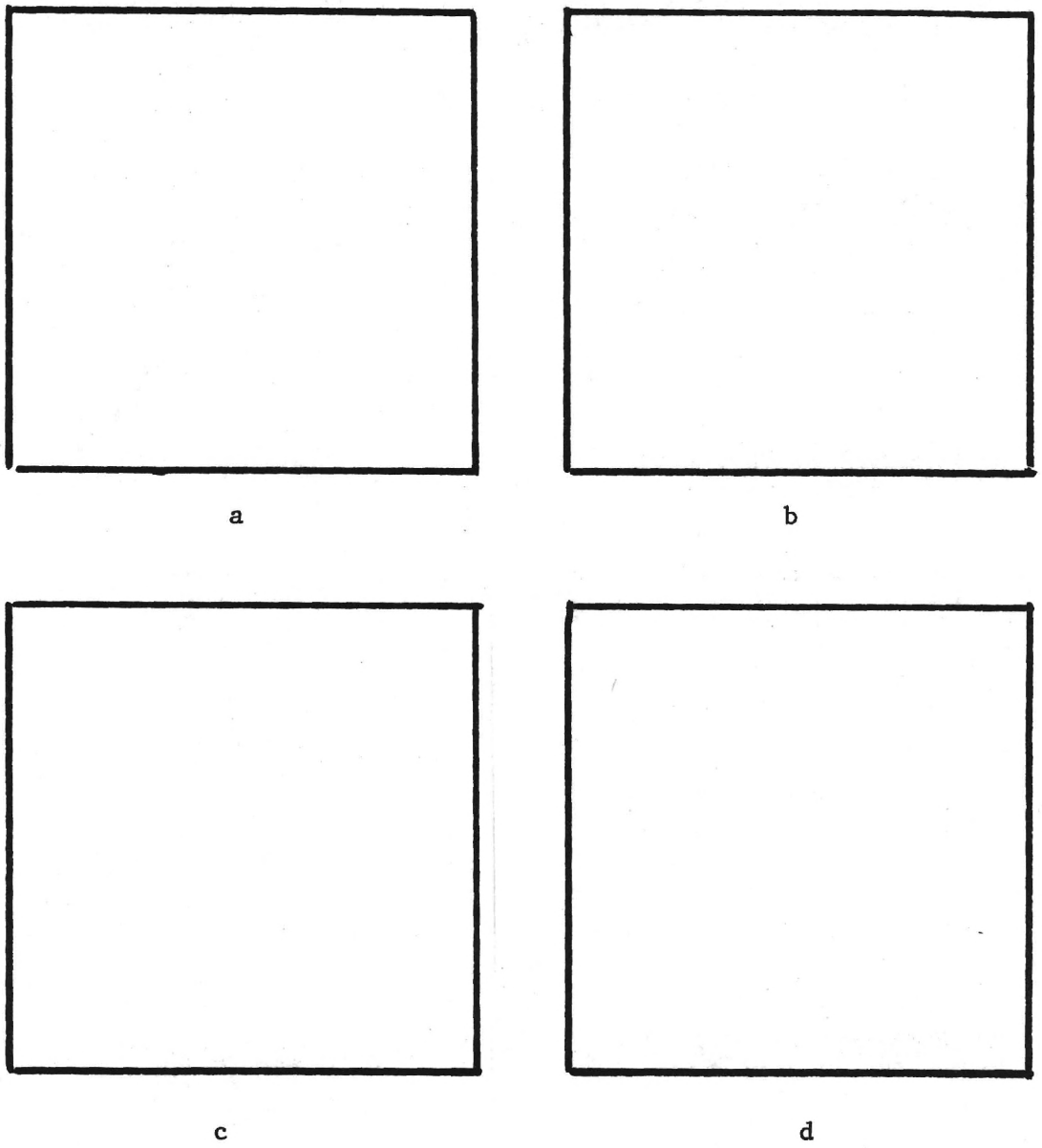


Fig. 37 Effect of a transverse gas flow on aluminum accumulates; A burning sample (a) is subjected abruptly to a small gas jet (b - d). In (b), the accumulates are dislodged, in (c) the accumulates are blown away, and in (d) the surface develops ripples.

of the aluminum and the protective oxide layer on the particle, assures that the aluminum will be resistant to reaction or vaporization under thermal conditions where the other propellant ingredients are rapidly decomposing. Further, the wetness of the binder surface during combustion (and to some extent, wetness of the AP surface) causes the non-reacting aluminum to linger on the surface before floating off into the high temperature gas field.

Because the propellant microstructure usually involves many small aluminum particles in the volume element of binder between larger AP particles, aluminum particles that linger on the wet binder surface are joined by underlying particles, leading to accumulation in a surface layer pattern initially consistent with the structure of the binder matrix. These particles usually become stuck together by wet binder, intermediate decomposition products of the binder, and by a sintering (cohesion) process involving aluminum leakage from the oxide coating, and bridging between particles (with oxidation in place).* At some point in the development of an accumulate, it becomes exposed to chemical species from the oxidizer, which may contribute to the adhesion-cohesion process. The relative contribution of each of these individual adhesion-cohesion processes is unknown, and presumably depends on many propellant variables, which in turn affect the nature of the accumulates.

Towards the end of the residence of the accumulate on the surface, it may be only tenuously attached there, and may extend outwards into flame elements of higher temperature and higher oxidizer content. With the ever-present drag of gases flowing out from the propellant surface,

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* Aluminum particles will also stick together at temperatures below the aluminum melting point in certain laboratory heating experiments (R-60), but it is not known whether this happens in the presence of binder melts observed on the propellant surface.

such accumulates will ultimately leave the surface, the timing being dependent on loss of attachment at the surface extremity, influence of gas motion in the combustor cavity, and sometimes by inflamation of the accumulate. Indeed, the ignition-agglomeration of the accumulate may become complete before separation from the propellant surface, and under certain conditions the aluminum combustion may proceed for a considerable time on the surface.

In general, the accumulate formation and behavior can be correlated with the propellant characteristics and combustion environment, with qualitative insight into the reasons for the behavior (5.3 - 5.5); considerably more basic information would be needed for realistic quantitative modeling or prediction of the behavior of novel propellants.

IGNITION OF ALUMINUM: AGGLOMERATES

6.1 Ignition - Its Meaning

The most conspicuous visual event in the behavior of aluminum in propellant combustion is the onset of luminous aluminum combustion. An irregular, greyish accumulate is transformed into a brilliant droplet with a glowing "comet-like" tail. Sometimes this occurs abruptly, either on the burning surface, at the moment of departure, or after the accumulate is free of the surface. Under other conditions (e.g., low pressure) the transformation to a burning agglomerate is resolved in the high-speed photography as a protracted and complex process, sometimes associated with the formation of flake accumulates or the break-down of complex filigree accumulates into agglomerate droplets. This variety of behavior can be correlated with the type of propellant, environment, and type of accumulate, at least for familiar propellants. Further, the behavior can be put on a fairly sound mechanistic basis if one considers what is known from controlled laboratory tests about the ignition behavior of aluminum as discussed below.

Aluminum will react vigorously with air - even at room temperature, provided the contact between metal and air is not impeded by the oxide coating that forms on the particles (very fine aluminum powder prepared in an inert atmosphere is pyrophoric, i.e., burns spontaneously, when dispersed in room temperature air). It is clear that the oxide skin inhibits ignition when present, but it ceases to impede combustion at the high temperature where it melts, and then the metal burns vigorously. It is no doubt important that the metal and its oxide (Al_2O_3) are insoluble in each other and that (in most atmospheres) the molten oxide tends to retract

from the surface of the molten metal (Fig. 2). This assures rapid exposure, heating, evaporation, and reaction of aluminum. There is not much controversy over the position that, at this point, ignition is accomplished if the atmosphere is oxidizing in nature. However, in the propellant combustion zone, the processes are usually many and complex between the time the aluminum particle is reached by the receding propellant burning surface and the time a burning droplet with retracted molten oxide is developed. Some of the processes involve aluminum oxidation after formation of accumulates, including particularly that time when breakdown of the oxide permits aluminum to flow as a result of surface tension forces. As will be seen below, a state of ignition may appear to exist at one location in an accumulate, and prove to be the source of a propagative "inflamation" of the rest of the accumulate or surrounding accumulates. This process involves progressive breakdown of oxide and flow of aluminum in the accumulate, due in part to heat produced by oxidation of the already inflamed part of the accumulate (Fig. 34,36). It is not clear how one should define the moment of ignition during this complex inflamation process, or that such a definition is even important. However the overall process is important because it affects the subsequent burning history of the aluminum, the responsiveness of the whole aluminum behavior to flow disturbances, and the nature of the Al_2O_3 product droplets. The inflamation process leads to a burning agglomerate droplet, and the process is affected by

the type of accumulate;

nature of the surrounding combustion zone environment (temperature, motion, composition);

physical properties of the aluminum and the oxide

(MP, BP, solubilities, surface tension, strength of the oxide);

chemistry of Al and Al_2O_3 reactions in the combustion zone environment

Until knowledge of these details is further advanced, understanding of the accumulation - ignition - combustion process will remain speculative, and depend heavily on observation of ignition in simpler situations, and on direct descriptions of the global aspects of the processes observable by combustion photography and quenched particle studies.

6.2 Ignition of Single Particles

Understanding of the ignition of aluminum accumulates is aided by the various studies of ignition and combustion of single particles in controlled environments. These studies (reviewed in (R-61)) include ignition by introduction of the particles into gas flames of controlled composition, introduction into pre-heated gas streams, exposure to intense radiant heating, and introduction as isolated particles in model solid propellants. Most of the observations made in such experiments were concerned with combustion rather than ignition, primarily because motion of the particles made observation of details of ignition difficult. Ignition delay times could be measured (R- 62), along with time resolved observation (R-63) of development of self luminosity (Fig. 38, 39). The ignition delay time was judged to be due primarily to time required for external heating to temperatures near to the melting temperature of the oxide (break-down of the oxide skin). The ensuing brief interval for development of steady luminosity is presumeably associated with further temperature rise, which is ultimately limited by equilibrium between the flame sheath around the

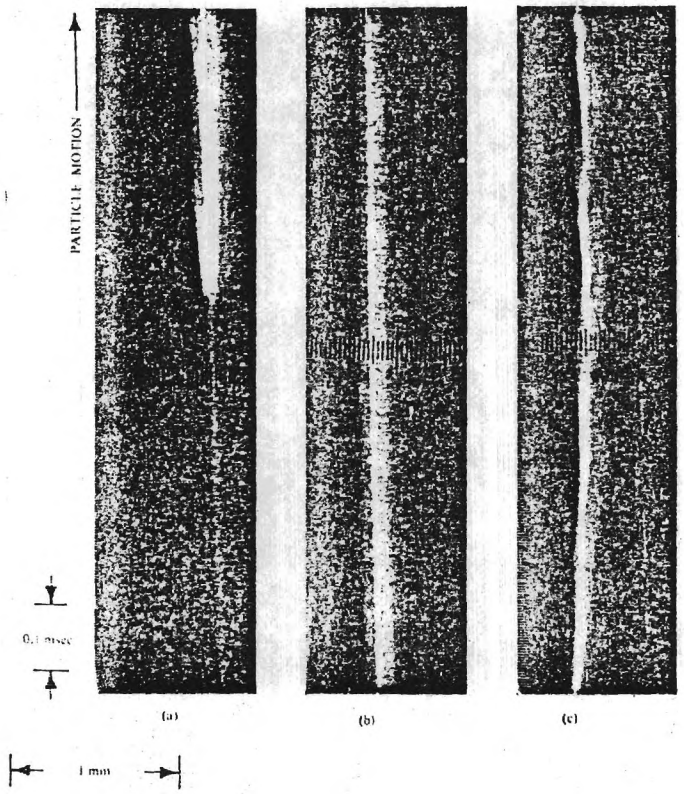

Fig. 38 Ignition - combustion of an aluminum particle in a gas burner flame, observed by still camera method.

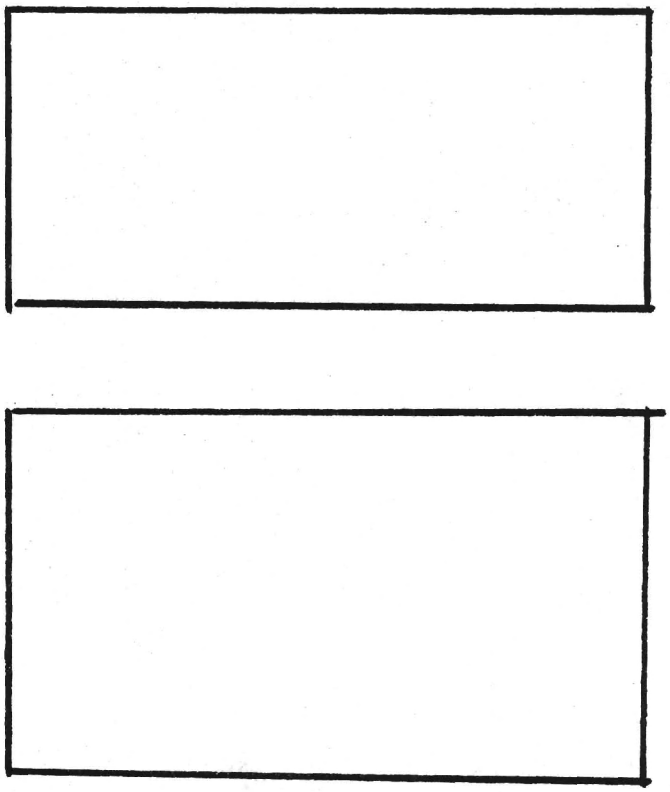

Fig. 39 Ignition of a single aluminum particle in CO/O_2 flame products, as shown by high speed motion pictures (gas flow downwards). Last 4 frames show ejection of an oxide droplet. Pressure one atm.

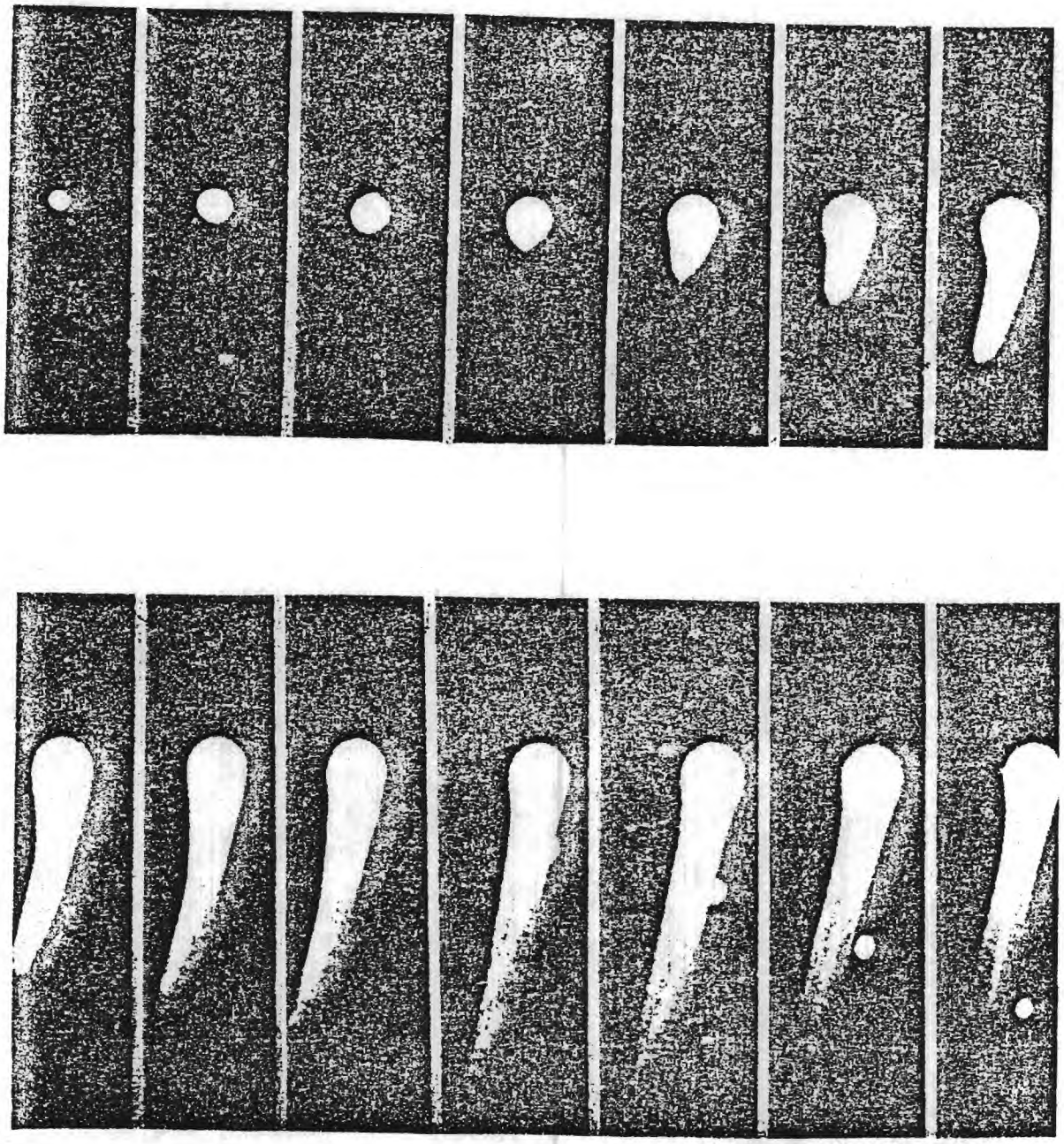

Fig 39

~~Fig 39~~. ~~Motion Picture Sequence of the Ignition of a Single Aluminum Particle in~~ CO/O_2 ~~Flame Products (gas flow downwards. Last 4 frames show ejection of an oxide droplet) atmospheric pressure.~~

droplet, oxidative heating on the droplet surface, and evaporation of aluminum. The few single particle experiments which have permitted successful observation of ignition by high speed photography were accomplished in situations where the particle was nearly stationary (R-63); such pictures (Fig. 39) show the particle beginning to glow, followed by sudden brigthening and enlargement of the image, indicative of development of a radiant flame envelope. Under some conditions one or more glowing droplets are ejected during this brief interval, droplets that are judged to be oxide rather than aluminum because of the quick decay in brightness and/or absence of smoke trail.

In general, the studies of ignition of particles in laboratory tests have not provided sufficiently high resolution to reveal the details of breakdown of the oxide skin, or of self-heating of the droplet prior to melting of the oxide skin (exception R-64). Some insight has been given from experiments in ignition of electrically heated wires (R-65), but the most significant observations of ignition are probably those made in conventional combustion photography of aluminized propellants, (Sec. 6.3), and those made in experiments on aluminum powder heated externally to temperatures below that required for self-sustained reaction (Sec. 5.3).

6.3 Ignition and Agglomerates

In an aluminum accumulate, the first indications of ignition are usually the appearance of self-luminosity in some portion of an accumulate, followed by a luminous smoke trail indicative of evaporation and gas phase*

* The reaction to Al_2O_3 in the detached flame is actually believed to be by by heterogeneous reaction on smoke droplets, which are the primary source of the self luminosity.

reaction of aluminum. This condition is accompanied by coalescence of the accumulate into a droplet, often in a propagative manner starting with the most luminous part of the accumulate. The onset of inflamation probably involves a combination of circumstances such as protrusion of the inflaming part of the accumulate into a high temperature and/or oxidizer-rich part of the combustion zone, presumeably after a period of growth of the accumulate, characteristic of the particular propellant.

Self-heating by oxidation can presumeably start at rather modest temperatures, since it apparently occurs to some degree in the process of sintering at around 670° C. However, there is very little unambiguous data on the behavior of accumulates subjected to continuing temperature increase. One may speculate that the oxide skin continues to crack or leak due to differential thermal expansion, with continued leakage and oxidation of aluminum. Atlernately (or concurrently), other reactions with aluminum or Al_2O_3 may occur involving H_2O, HCl, ClO_3, etc. The reactions may reduce the protectiveness of the oxide coating, or simply supply more heat (or both).

Relative to the breakdown of accumulates, it should be recognized that a sintered accumulate should have a unique attribute of flame propagation, due to the structure, comprised of particles (droplets) interconnected by a complex oxide network. When one particle (droplet) starts to oxidize, it does not lose heat rapidly to neighboring aluminum because of the low thermal conductivity of the oxide interface between particles of the accumulate. Thus the particle may reach the melting point of the oxide coating and become fully ignited, while the rest of the accumulate is still producing relatively little self-heating by its own oxidation. The intense heat from the burning "particle" melts the oxide on adjoining

particles (Fig. 34,40) leading to ignition of those particles, and propagative inflamation of the entire accumulate. This process is, of course, abetted by a "near to ignited" condition of the whole accumulate, a condition that would prevail if the accumulate had survived on the burning surface for a period of time approaching that typical for surface residence of aluminum for that propellant and environment. In practice, one does indeed see sintered accumulates, propagative inflamation of accumulates, and a measure of periodicity of shedding of aluminum at any local site on the burning surface, consistent with the above arguments. However it would be rash to claim that the argument is complete or always applicable, and indeed in other situations, accumulates leave the surface prior to ignition, or ignite so abruptly that details of the process cannot be resolved. However, it seems likely that the physical nature of the accumulate plays an important role in ignition, often leading to propagative inflamation, which in extreme cases (e.g., periodic combustion of dry-pressed AP-Al pellets) involves progressive surface-wise inflamation of an entire burning surface (window bomb sample, i.e., 1/4" square (R-66)).

During the inflamation of an accumulate, the molten aluminum escapes the confines of the oxide coating, and adjoining parts of the accumulate become drawn together by surface tension. The result is a growing droplet of reacting aluminum, referred to in this report as an agglomerate. The ultimate size of the agglomerate is determined by the size of the parent accumulate, plus any neighboring aluminum picked up during the mobile period of the accumulate evolution and inflamation. Thus the agglomerate size is linked back to propellant ingredients and combustion environment through the accumulate development described in Sections 5.2 - 5.5. These

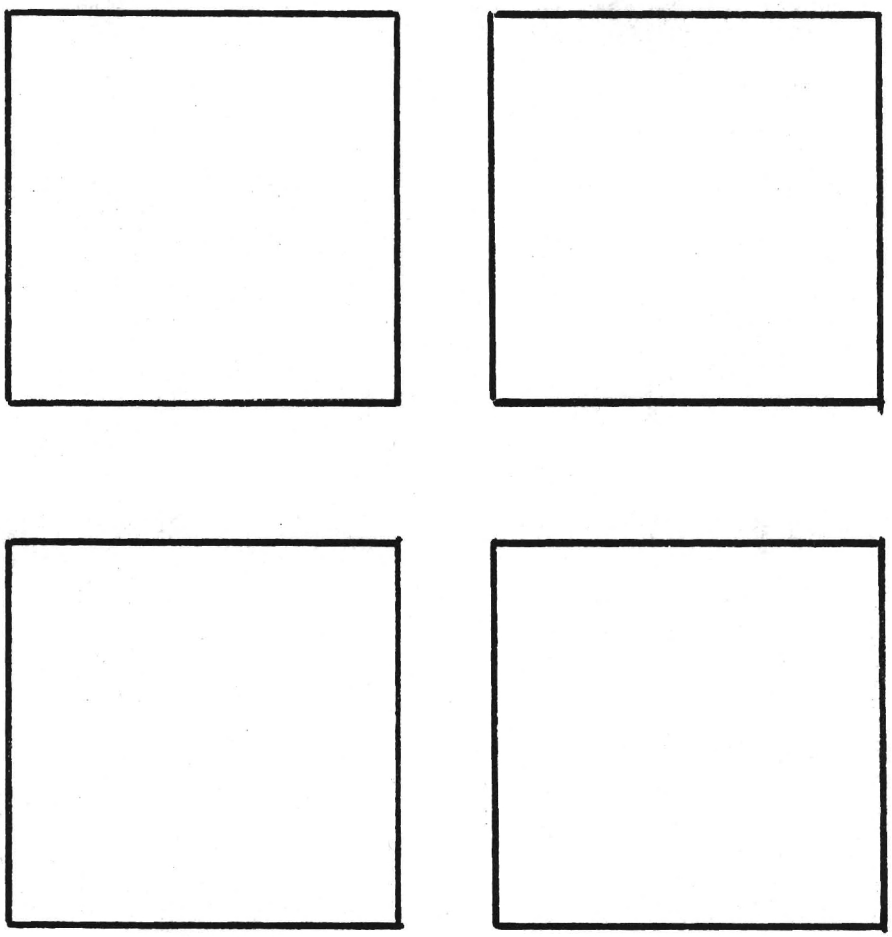

Fig. 40 Sketch of inflamation of a sintered accumulate.

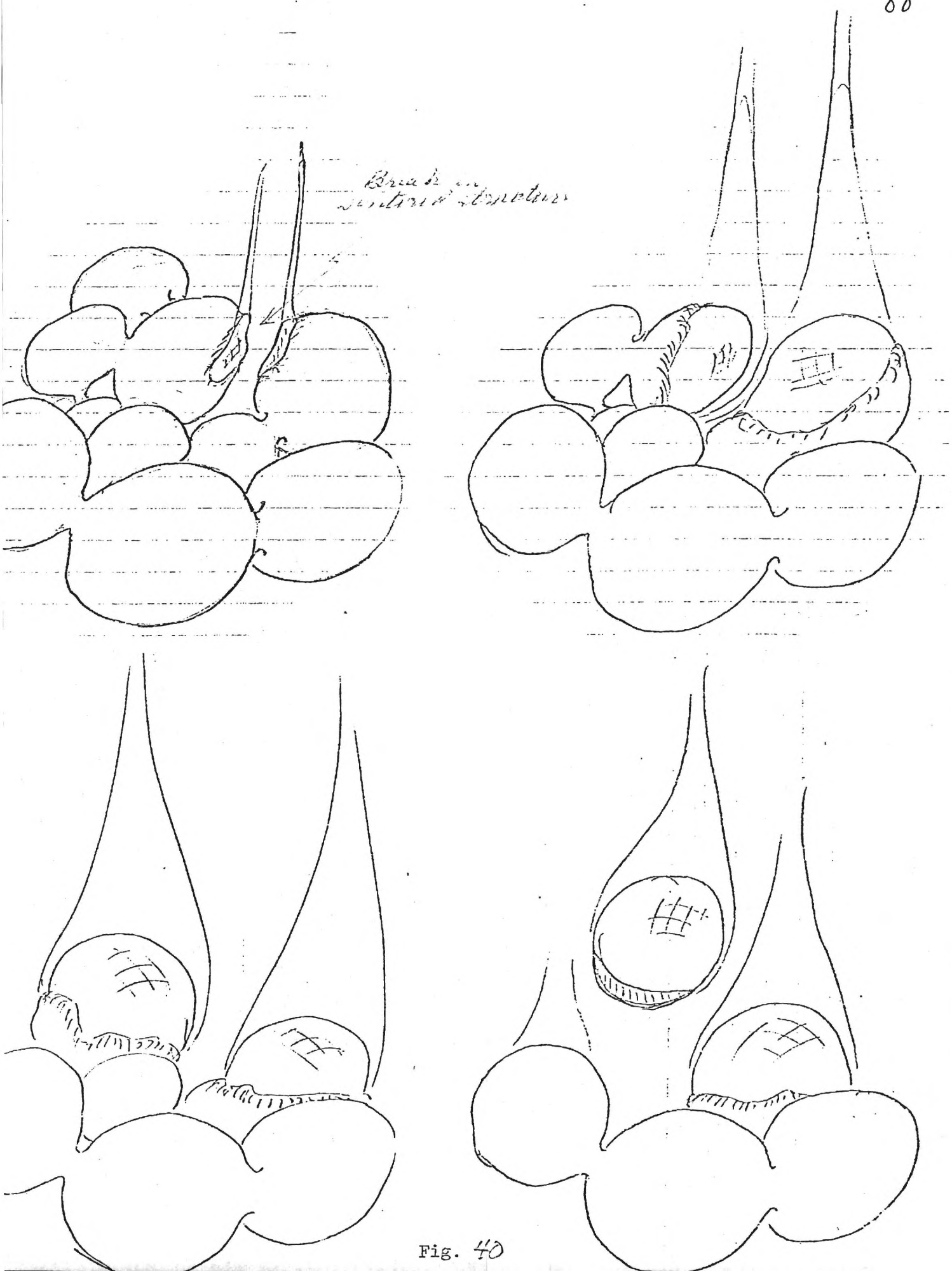

Fig. 40

agglomerates represent the majority of the ingredient aluminum, still unreacted, and usually fated to burn in the gas flow field in the rocket motor, much like the fuel droplets in a liquid propellant rocket motor. Alternately, agglomerates sometimes remain and burn on the propellant surface, although this is not typical except when inertial forces (e.g., in spin-stabilized rockets) resist departure from the surface (R-67).

The detailed nature of an agglomerate is unknown. It is usually assumed that it consists of an aluminum droplet with one or more lobes of retracted Al_2O_3 as in the case of combustion of single aluminum particles (R-68) in air atmospheres*. Burning agglomerates appear to be of this form in combustion photography of propellants as well (Fig. 2). However, the transition from accumulate to burning agglomerate is necessarily complex, given the complexity of the accumulate itself, and its pre-ignition and ignition environment. Agglomerates that have been quenched immediately after (or during) ignition are found to be brittle, with heterogeneous interiors (R-69), suggestive of internal impurities such as carbon. In addition, it seems unlikely that the extensive structure of Al_2O_3 in the original accumulate is fully retracted by the time the agglomerate is formed, so early-quenched agglomerates would be expected to include internal Al_2O_3 structures until the oxide has had time to withdraw from the interior of the droplet by some as yet undetermined mechanism (Fig. 41). In a sense, this is all part of ignition, but there seems to be no virtue at present in quibbling about the definition, so long as the recognized qualitative aspects of the process are described.

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* Even in this "simple" situation, the oxide lobes appear to contain nitrogen.

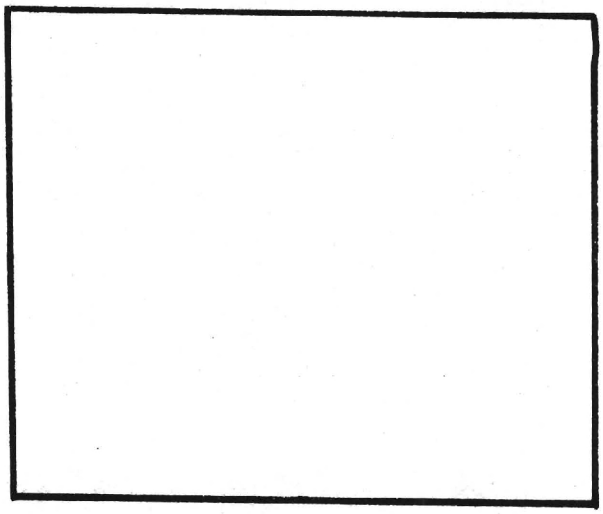

Fig. 41 An accumulate quenched in the process of transformation to an agglomerate. SEM of typical particle obtained by burning a propellant under liquid nitrogen.

6.4 Relation of Ignition - Agglomeration to Type of Accumulate, Environment, Propellant

As suggested earlier, the ignition-agglomeration process of various types of accumulates can be related by experience and mechanistic reasoning to the types of accumulates described in Sec. 5.4.1 to 5.4.5. Thus the smooth accumulate layers typical of propellants with fine AP, burning at low pressure (Sec. 5.4.1) form flake accumulates that tend to curl up out of the surface (Sec. 5.5), and ignite along the edges of the flake (Fig. 34). The ignition is propagative, typically along the edges of the flake. The molten aluminum draws together, along the raised edge of the flake, apparently reacting and self-heating the rest of the accumulate in a propagative fashion until the entire flake is ingulfed and forms an agglomerate that floats away from the surface (i.e., in the combustion window bomb). At higher pressures, or with burning rate catalysts, the details of accumulate formation and ignition are contracted, both in space and time. Then ignition appears to occur abruptly, at the moment of separation from the surface layer, and encompassing a smaller accumulate. Details are difficult to resolved under these conditions (Fig. 31).

The irregular accumulate layers typical of coarse AP (Sec 5.4.2) tend to break away from the surface with considerable remaining rigidity, but inflame propagatively from one or more initiation point in the accumulate (Fig. 36). The inflamation may occur on the burning surface or in the process of moving away. When it occurs on the surface, the inflamation gives the impression of high mobility of the ignited part of the accumulate, especially when viewed by self luminosity. However, such motion usually consists of either agglomeration during propagative inflamation (i.e.,

coalescence of the accumulate), or motion of the entire accumulate as it loses constraints to the surface. Under adverse ignition conditions (e.g., low pressure), the ignition may be delayed until after the accumulate has left the surface. Under those conditions the details of ignition are not so well resolved in motion pictures because of rapid motion, but the ignition event is more abrupt.*

The more typical accumulate behavior described in Section 5.4.3 arises from accumulates of modest size or favorable ignition conditions (e.g., high pressure, high AP content). Ignition (i.e., total inflamation of the accumulate) occurs rather abruptly (a few milliseconds). Usually this is concurrent with separation from the burning surface, with the combined event occurring too rapidly to provide basis for speculation about cause and effect (similar to Fig. 31). It may be significant that the burning agglomerate sometimes (i.e., with some propellants) does not leave the surface immediately after ignition (Fig. 42) suggesting that the abrupt ignition is not necessarily due to emergence of the accumulate into the main diffusion flame. On the other hand, abrupt ignition of accumulates, usually accompanied by departure from the surface, is typical of catalyzed propellants (Fe_2O_3 or copper chromite), and these catalysts are believed to bring the diffusion flame closer to the surface, a relation suggesting that the abrupt accumulate ignition is due to high heating rate from the diffusion flame.

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* Perhaps even more so in a motor, as dilution of the combustion zone by the flushing flow of nitrogen probably retards ignition in window bomb tests at locations more removed from the burning surface.

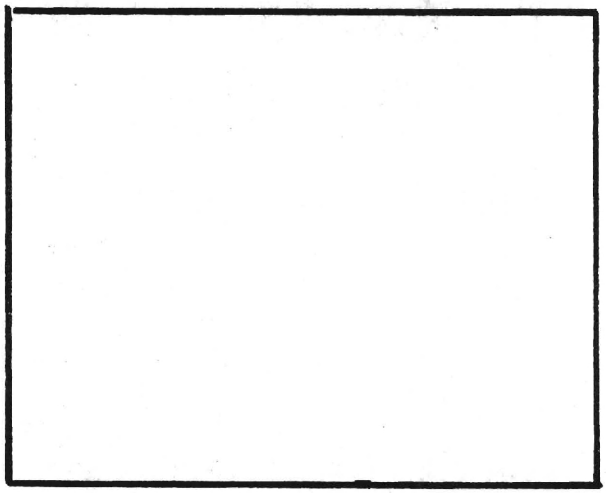


Fig. 42 Ignited agglomerates, lingering on the surface.

Ignition of aluminum accumulates in composite propellants with double base binders is as varied as the accumulate behavior itself (Sec. 5.4.5. **The igniting flake behavior described above has been observed** with formulations having fine AP and smooth accumulate surfaces. Coarse AP caused irregular accumulates, with ignition starting at one location and inflaming the entire accumulate. As noted before, the accumulates occurring with this type (Fig. 33) of propellant tend to persist on the burning surface with rather tenuous attachment. With this type of propellant, ignition typically starts in that portion of the accumulate most remote from the propellant surface (presumeably in a location most exposed to the gas phase exothermic reactions) (Fig. 43). The ignition then propagates through the accumulate towards the burning surface until the entire accumulate (and sometimes its neighbors) have ignited and agglomerated. Under adverse ignition conditions, the accumulate may more typically leave the burning surface unignited, and ignite as it moves out **in the high temperature flame zone. With AP content or high solids content, ignition is more vigorous and occurs on the burning surface, with less accumulate growth before ignition.**

6.5 Summary

From the foregoing it is clear that the concept of ignition is not a very precise one when referred to ignition of aluminum. However, a significant body of information exists on the transient processes leading to complete inflamation. In the case of single particles, breakdown and melting of the oxide coating is a necessary step in reaching full combustion rate. In laboratory tests on clusters of particles, partial breakdown of the oxide coating (e.g., by differential thermal expansion) can lead to flow and agglomeration due to surface tension of the molten aluminum, especially in an atmosphere with low concentration of oxidizing species. The same effect is

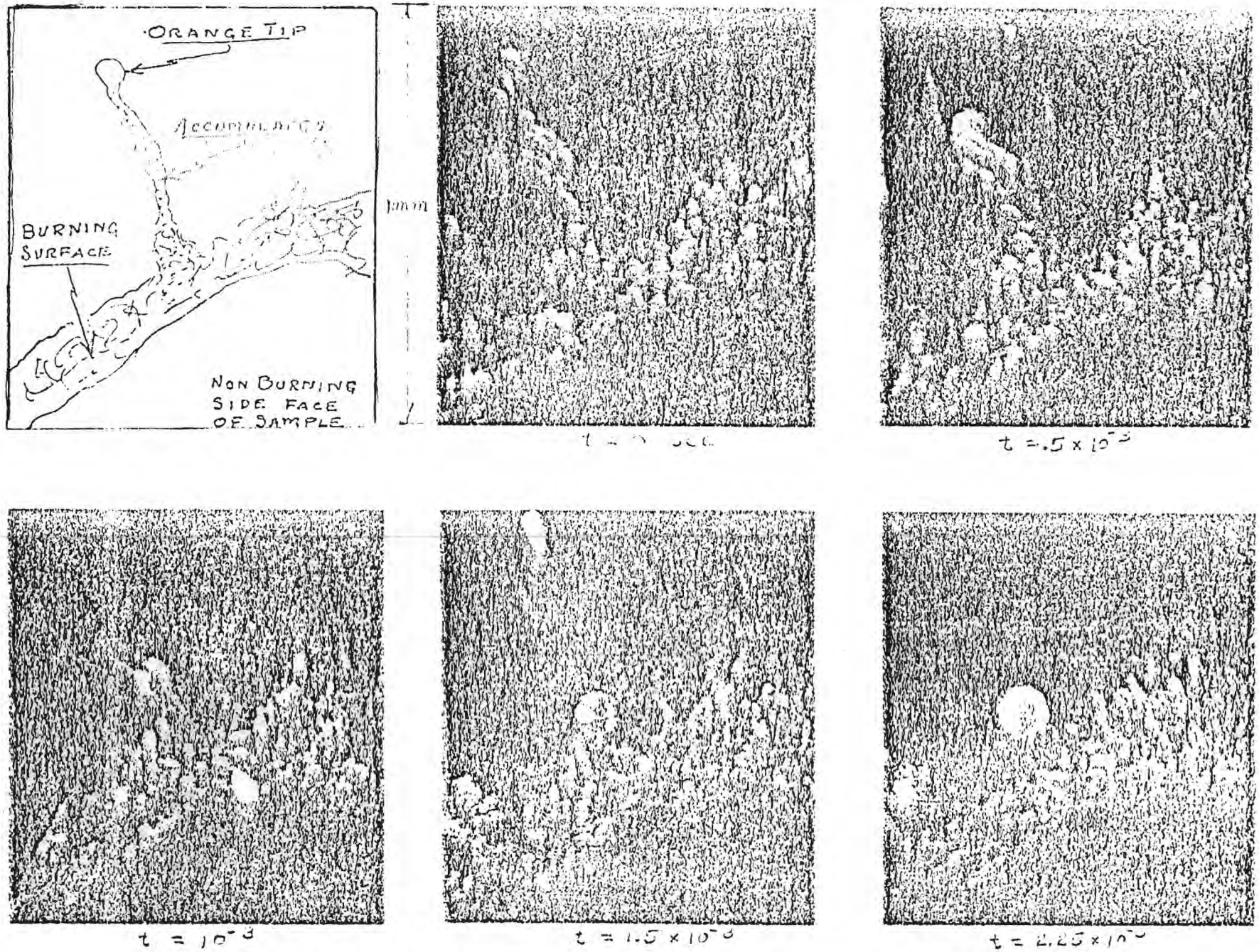


Fig. 43 Ignition of a filigree accumulate from the top down, illustrating the role of the high temperature flame in aluminum ignition: CMDB propellant, 300 psia.

minimized in an oxidizing atmosphere because of the formation of new oxide on the surface of exposed aluminum. However the new oxide can cause sintering of clusters.

In the propellant combustion zone (particularly AP/HC/Al propellants) the aluminum clusters exist initially in a fuel atmosphere with temperatures below the aluminum melting point. The structure of the combustion zone is such that attainment of higher temperatures occurs concurrently with exposure to oxidizing species; agglomeration is apparently delayed due to continued formation of protective oxide until temperatures well above the melting point of the aluminium prevail. During the intervening time, sintering apparently occurs, with ignition being delayed until more decisive break-down of the oxide coating occurs. A variety of processes may be involved in this break-down, but they are usually followed by a precipitous process, i.e., local melting of the oxide, exposure of aluminum, and rapid local heat release.

Because the heat release following break-down of the oxide coating is sufficient to melt the oxide on neighboring parts of an accumulate, the local ignition is propagative, and the aluminum proceeds to agglomerate as rapidly as ignition propagates into the accumulate. This continues until the accumulate is fully engulfed. If one had to define a moment of ignition, it probably should be when the oxide is melted sufficiently in some locality of the accumulate to start propagative inflammation and agglomeration. This situation is clearly visible in motion pictures of combustion with some propellant-pressure combinations (Fig. 1, 34a, 43), and is signaled in

other situations as well by the appearance of the oxide smoke trail produced by detached flames adjacent to aluminum surfaces (Fig. 1, 2, 32, 34, 42; also Sec. 7).

Depending on the propellant and combustor environment, the ignition-agglomeration process may start while the accumulate is still on the burning surface, while it is leaving, or after complete separation (Fig. 15, Sec. 5.1). Although mechanistic understanding has not reached the level of quantitative expression or prediction of behavior of novel propellants, the combination of understanding and accumulated observations provides a basis for rational correlation of propellant variables, accumulate formation, and the ignition behavior: in other words, the path (or paths) in Fig. 15 most typical of a given propellant-combustor environment combination can be forecast with reasonable certainty for familiar propellants and moderate variants thereof. Perhaps the most risky aspect of this generalization is the case of effects of ballistic modifiers, which have not been studied systematically and which act by undetermined mechanisms. Different trends may occur when AP content is low, and possibly also with formulations involving two widely different AP particle sizes (where aluminum produces large effects on burning rate: Ref. 70).

ALUMINUM COMBUSTION AND PRODUCTS

7.1 General Situation

To this point the discussion has involved mostly aspects of aluminum behavior that would be of little or no interest if they did not affect subsequent processes. The object of inclusion of aluminum in the propellant in the first place is to burn it, transfer the heat of reaction to low-molecular weight species in the propellant products, and convert that energy to kinetic energy in the rocket nozzle. The preoccupation with details stems from the fact that aluminum, unlike other propellant ingredients, does not decompose or vaporize and react immediately adjacent to the burning surface, and does not ordinarily form a gaseous reaction product. These peculiarities, common to many metal fuels, are further complicated by the formation and nature of aluminum oxide on the metal particles before ignition, which drastically modifies the kind of aluminum particle that ultimately ignites and burns in the rocket motor volume.

In the preceding Sections, the complex behavior of aluminum has been traced up to the formation of accumulates of hundreds and thousands of original aluminum particles, and to the onset of burning of accumulates. With most propellants, the aluminum leaves the propellant surface once burning is established, and it then burns as it travels through the volume of the combustion cavity. There, one becomes concerned with completion of combustion before discharge through the nozzle, with dynamic response of the combustion to flow disturbances, and with the size of the Al_2O_3 droplet products (which affects damping of gas flow disturbances (R-71) and propulsion efficiency of the two phase flow in the nozzle (R-72)). The general problem of distribution of burning

droplets and products in the combustor cavity has received only superficial study, but it is clearly a matter of concern. Unlike the parallel problem in liquid propellant motors, concern is primarily for the early part of the motor burning period when combustor cavity volume is low. In practice, the problems are also more persistent when aluminum combustion conditions are unfavorable, such as at low operating pressure, high aluminum concentration, or with extremely oxidizer-deficient propellants.

In order to understand the state of knowledge of agglomerate combustion and the reasons for the particular research that has been done, it may be helpful to re-emphasize some aspects of the situation. One would like to be able to forecast how an agglomerate would burn. But the true nature of an agglomerate is not really known. The combustion will be discussed here first in terms of experiments on aluminum droplets of less complex origin, but direct evidence shows that agglomerates are structurally and chemically complex, at least during the initial phase of their burning (R- 73) and this subject will also be discussed.

A second factor in understanding (or non-understanding) of agglomerate combustion is the observational difficulty resulting from high velocity and small size of the burning agglomerates, and from obscuration by the Al_2O_3 smoke produced in the combustion. Every effort to circumvent this problem leads to questions as to the relevance of experimental results. This will become evident in the following, but it is probably desirable to stress here the conditions in the rocket motor that may need to be simulated in laboratory experiments to assure complete relevance. Such experiments should ideally include:

a. An initial particle like an agglomerate

b. A convective flow typical of the agglomerate trajectory in a motor

c. A chemical environment containing the appropriate amounts of active species, in which H_2O is probably the principal oxidizing specie, with depletion of oxidizer, as occurs along the agglomerate trajectory in the motor

d. A radiation environment simulating that along an agglomerate trajectory

e. An environmental temperature roughly like that in a motor.

Because of the observational difficulties in a motor, and the difficulty of simulation, most experimental results are from experiments in which simulation is clearly lacking or observations are potentially misleading. In spite of this, a very respectable body of knowledge has been accumulated, from which reasonable speculations can be posed and from which reasonable experiments and analytical models can be designed. These results will be discussed briefly in the following, but with due regard for questions of simulation and limitations of observation.

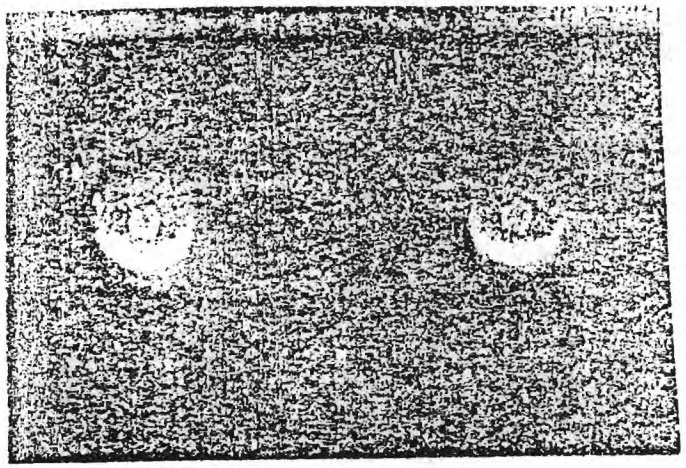
7.2 Aluminum Particle, Controlled Atmosphere (APCA) Tests

The majority of relevant information on aluminum combustion has been obtained from experiments that ignite single aluminum particles or wires in controlled atmospheres. Such experiments permit study of particle size and atmosphere effects, and provide for photographic and quenched sample studies. The most extensive tests are those (R-74) involving radiation pulse ignition, with burning droplets then falling

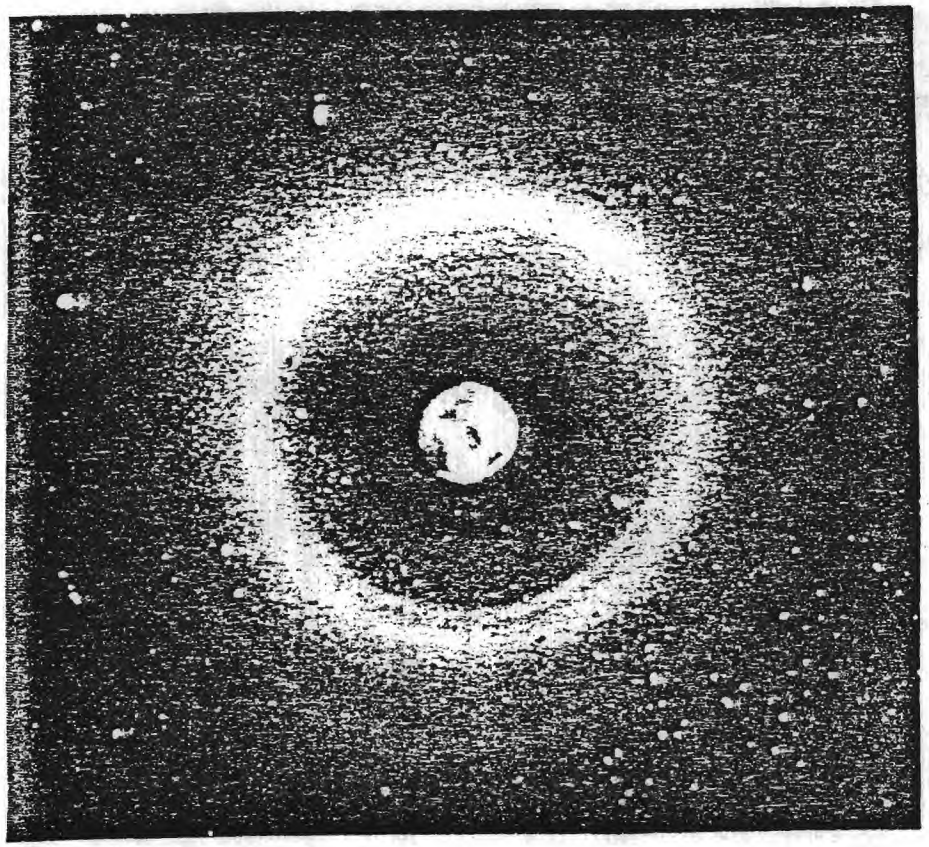
in a quiescent room temperature atmosphere. The most relevant tests are probably those in which observations of combustion are made with a propellant having a few aluminum particles of desired size (R-75). Useful tests have also been run in apparatus to provide a gas flame environment (R- 76).

Collectively, the APCA tests show a variety of combustion behavior, of uncertain relevance to rocket motor combustion. It seems clear that the aluminum particles burn with a veil of oxide product droplets, which coincides with the primary combustion zone (Fig. 2, 44). Single particle tests lend themselves readily to measurement of burning times, by measurement of streak photographs (Fig. 45) or luminosity-time records (Fig. 46).

Under various conditions, many other phenomena are also exhibited, such as ejection of oxide droplets or bubbles (R-77), encapsulation of the aluminum by oxide (R- 78) and fragmentation. The dependence of behavior on atmosphere is suggested by the examples in Fig. 47 (R- 79), which show luminosity vs. time for single droplets burning in various atmospheres (ambient temperature and pressure). Observations of quenched samples collected during various single particle tests, indicate that the detached combustion zone with fine Al_2O_3 smoke is common to all combustion environments, but that the nature and effect of oxidation and accumulations of oxidation products on the droplet surface is very dependent on the atmosphere, and that oxide, oxynitride, or Al-O-C complexes (R-80) on the surface is responsible for the irregularities in the luminosity in Fig. 47. It is not yet clear what behavior is typical of propellant combustion, but



(a)



(b)

Fig. 44 Evidence of the veil of oxide smoke in the detached flame: Part a, a high speed motion picture of an aluminum droplet burning in an argon-oxygen atmosphere; Part b, photomicrograph of the droplet-smoke sample resulting from quench of an aluminum droplet burning in an argon-air atmosphere.

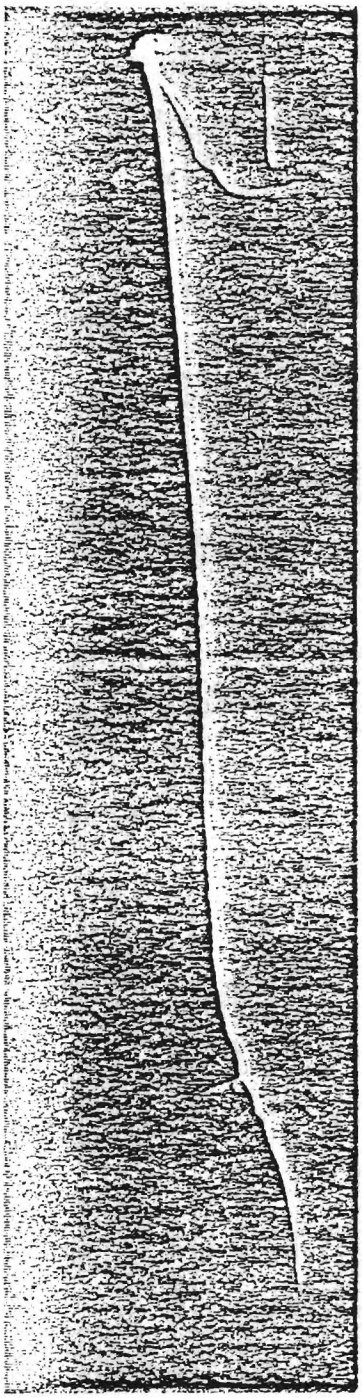


Fig. 45 Streak photograph of aluminum droplet burning history in dry air. Camera shutter is open for duration of burning of the droplet as it falls through the test atmosphere.

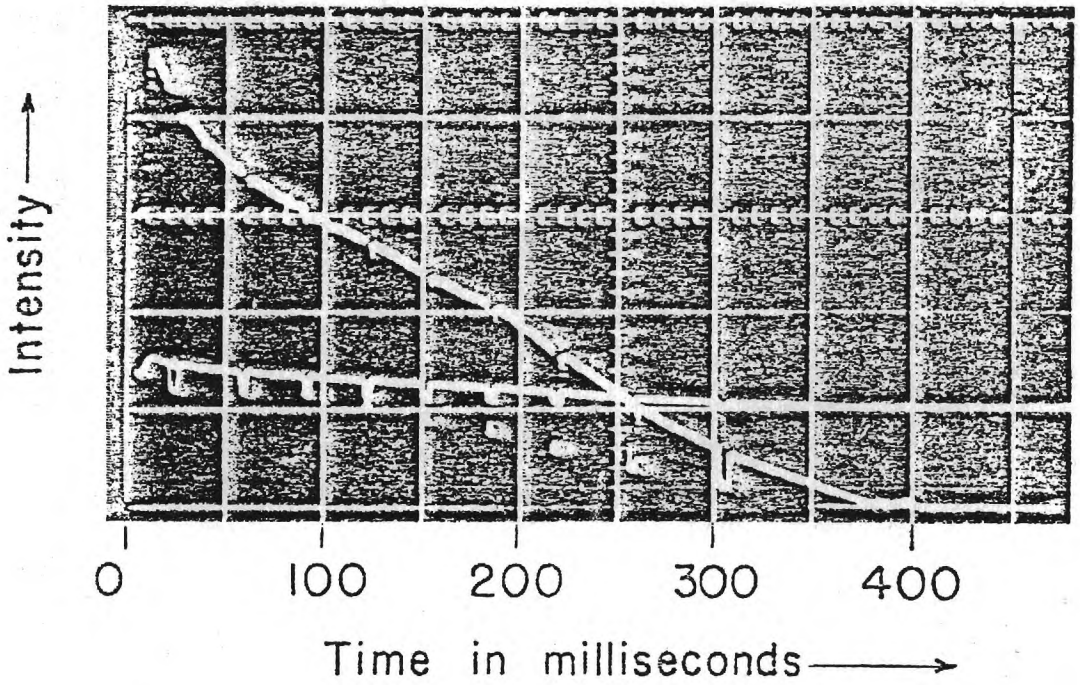


Fig. 46 Luminosity-time record for an aluminum droplet burning in a dry 20/80 O_2/Ar atmosphere. Dips in the trace are position markers.

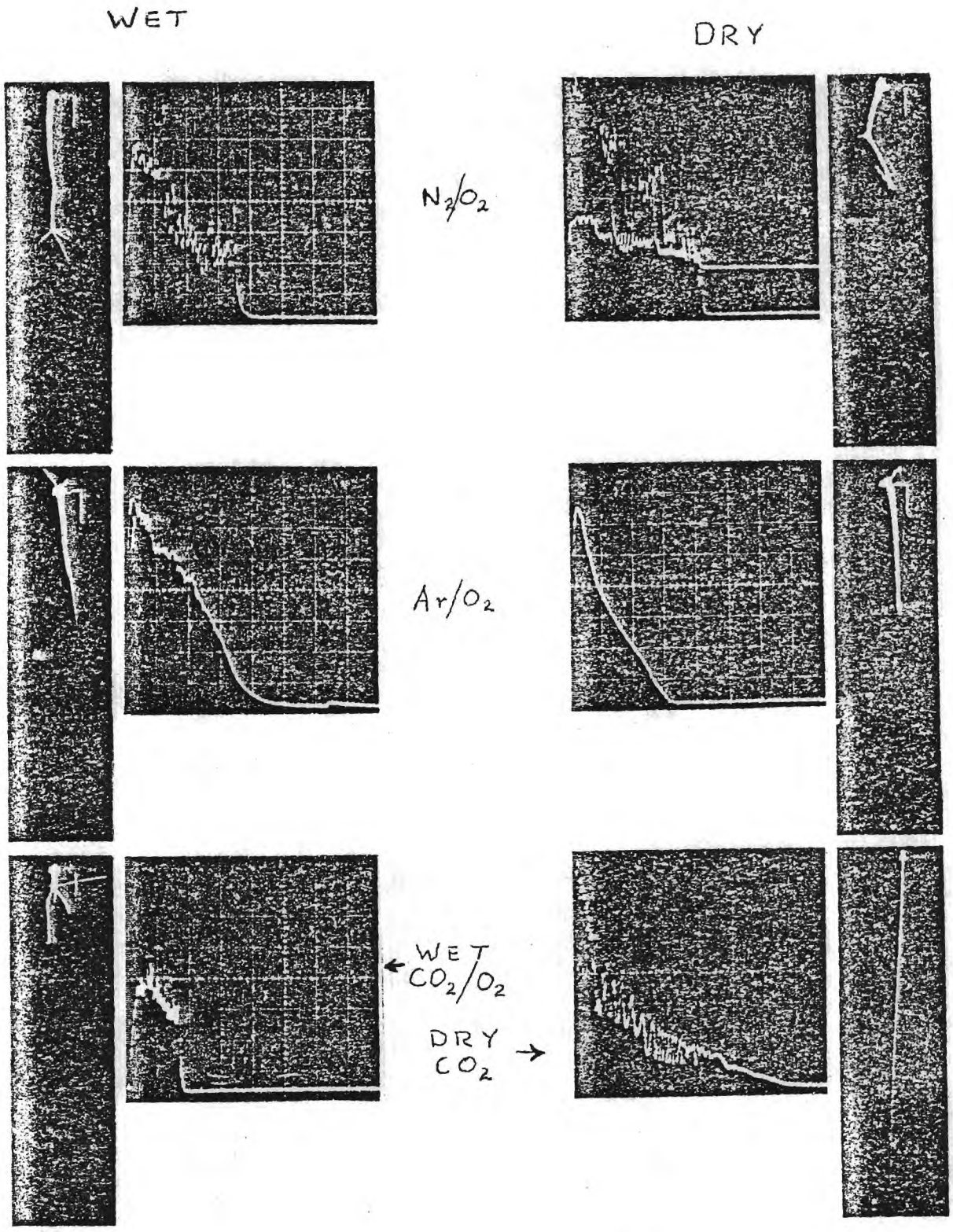


Fig. 47 Still plate track photos and photomultiplier emission (luminosity) traces of aluminum droplets burning in various atmospheres (room temp; 1 atm pressure).

it is clear that the detached flame-smoke veil is typical and that some surface oxide accumulation also occurs (Fig. 2; R-81). The irregular behavior seen in so many single particle-tests has not been reported for most propellants, but available observations are not sufficient to prove that such behavior does not occur; it is clear that surface oxidation often (or possibly always) occurs. This will be commented on often in the following.

Particle combustion experiments in gas flames provide closer simulation of the atmospheric enviornment in propellant combustion than is possible in the cold gas experiments, while retaining much of the convenience of those experiments. Observations have been made by streak photographs (Fig. 38) (R- 82), motion pictures (Fig. 39) (R- 83), and quenched samples (Fig. 48, 49) (R- 84). The presence of the detached flame and veil of oxide smoke is re-emphasized by this work, along with formation of oxide on the droplet and a variety of corresponding combustion irregularities (R- 85). Fragmentation was a common occurrence, but appeared to be absent in flames with low free oxygen similar to propellant flames (R- 86). Droplet burning times have been measured under various flame conditions (Sec. 7.4).

The nearest reported approach to motor conditions that preserved acceptable viewing conditions was accomplished by burning propellant samples that have isolated aluminum particles of preselected size (R- 87). Observations were made primarily by photographic methods. Unfortunately this type of aluminum particle combustion experiment has not been used extensively, although it permits relatively good simulation of motor

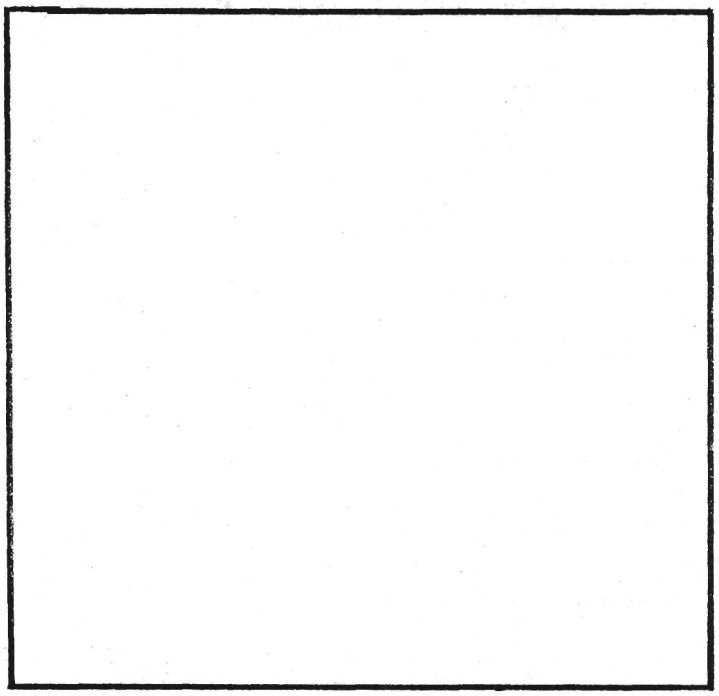
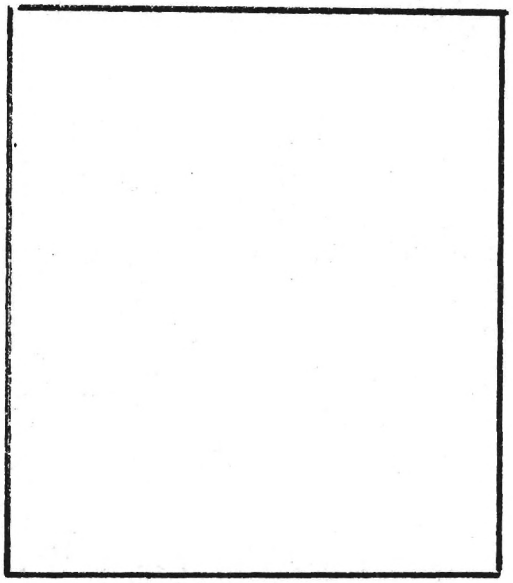
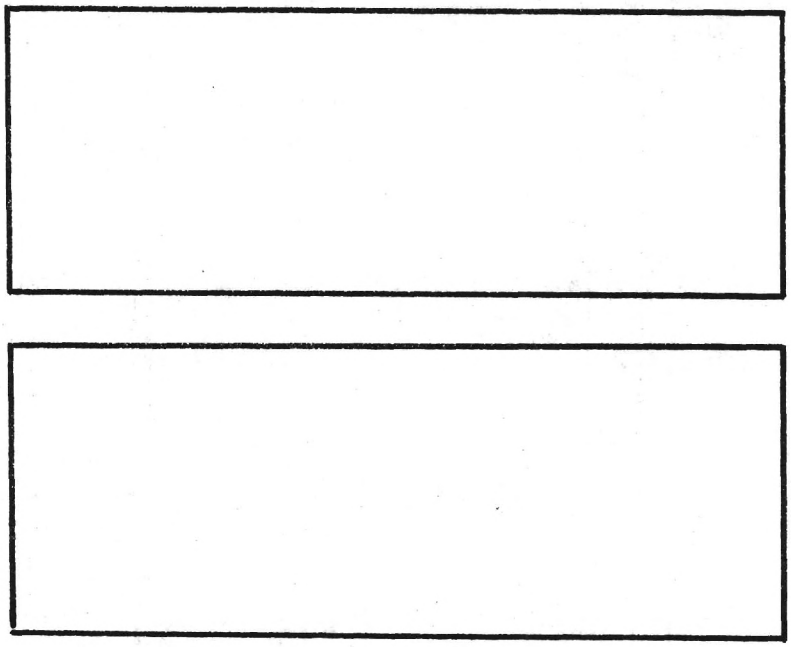


Fig. 48 The veil of oxide smoke from the detached flame, as shown by sample from a quench plate test in a CO/O_2 flame (photomicrograph of droplet and smoke cloud that impinged on quench plate).



49 a



49 b

Fig. 49 Nonsteady processes occurring during burning in gas burner atmospheres: Part a, Spiraling motion due to droplet asymmetry (presumably due to oxide lobe: 'tubular appearance of the projection of the spiral illustrates the detached and concentrated nature of the flame); Part b, Ejection of oxide droplets early in burning (hydrogen-oxygen flame, 70 μm aluminum particles).

pressure and chemical environment.* Although tests have not been sufficiently comprehensive to be fully convincing, they indicate that combustion is similar to the other single particle experiments, except that irregularities such as fragmentation are not conspicuous (R-88). It is speculated that high temperature and pressure are conducive to more regular burning. The typical detached reaction zone with fine smoke (Al_2O_3) is evident, as are the coarser oxide particles (in collected products).

In summary, the single particle tests indicate persistent presence of the detached reaction zone-flame envelope with fine oxide smoke formation; usual presence of surface oxidation-oxide accumulation on the aluminum droplet surface; and a variety of puffing, spinning and fragmentation phenomenon which appear to be less conspicuous under more rocket-motor-like conditions. These tests provide droplet burning time data that will be discussed later; accumulated evidence suggests that droplet burning times are of the same order as stay times in the combustor under some conditions of interest, implying volume-distributed combustion and risk of incomplete combustion. Descriptions of the two-phase flow in the motor must give consideration to both the distributed combustion and the "bimodal" nature of the Al_2O_3 product population and its dependence on the overall behavior of aluminum in the combustion zone.

7.3 The Initial Phase of Agglomerate Combustion

Returning to the combustion of conventional aluminized propellants,

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* Assuming mixing with an environmental gas is delayed until aluminum droplets are burned, a condition not usually achieved.

it was noted in Section 6 that ignition and agglomeration are concurrent parts of a complex conversion from accumulate to burning droplet. Ignition may be convincingly accomplished before agglomeration of the accumulate is complete. Indeed there is some uncertainty as to the true nature of a burning agglomerate, especially early in its burning history (and thus some uncertainty as to where agglomeration is "complete". Not only are the relevant experimental observations of geometrical, physical and chemical state of agglomerates sparse and indecisive, but the conditions leading to the agglomerate give the opportunity for a very complex entity. In the initial phase of agglomerate burning, it is reasonable to assume that the "droplet" may contain some material other than Al and Al_2O_3, and that the Al_2O_3 may not have fully redistributed itself from its original intricate filligree of sintered shells. The available information on the formation and initial phase of burning of the agglomerate comes from two sources, combustion photography and studies of quenched agglomerates. Results are not entirely consistent.

Combustion photography shows the agglomerates starting from the accumulate stage on the burning surface and shows their behavior until they become obscured by the Al_2O_3 smoke cloud or their own flame sheath. This observation usually occurs within 2500 micrometers of the propellant burning surface. At modest pressure (e.g. 10-30 atm), agglomerates in the 100 to 500 micrometer diameter range appear to be converted into molten droplets with oxide lobes, much like those seen in laboratory experiments on single aluminum particles. Because of the limitations in resolution in the photography (roughly 20 micrometers), and the rapid motion, photography has not revealed much about small agglomerates (although one might

suppose that they would go through the transition from accumulate to aluminum droplet more rapidly than large agglomerates).

The molten droplet-oxide lobe appearance is particularly manifested by the following observation in combustion photography. The agglomerates exhibit highlights from reflection of the external light source, suggestive of a molten surface. The "oxide lobe" is very bright, suggestive of the high emissivity of Al_2O_3. Collisions of agglomerates result in abrupt (surface tension driven) coalescence and immediate transition to spherical configuration, suggestive of liquid droplets. Such impulsive coalescence has been seen to result in momentary oscillation of the product droplet, suggestive of droplets with low internal friction, surely free of any extensive structure of residual solid accumulate oxide. A supporting observation concerns those fairly rare instances where aluminum puddles occur on the burning surface after ignition (e.g., with polimide binder R- 89): in such instances the agglomerate is sufficiently liquid to flow out and conform to the geometrical irregularities of the burning surface, still showing discernible boundaries between molten aluminum and overlying lobes or patches of oxide. Collectively, these observations suggest that the aluminum from the accumulate quickly becomes a single, liquid droplet, with external lobes of oxide. It does not determine whether the liquid aluminum has soluble impurities, or how much oxide is present in the lobe, or how rapidly the oxide is increasing, or whether the lobe is all oxide.

Isolated observations of agglomerates quenched early in burning yield particles of complex internal geometry (Fig. 41, R- 90), particles that are brittle (R-91), quite unlike aluminum particles. Because of the difficulties in quenching and sampling close to the burning surface,

it is uncertain whether the observed samples are typical, and whether their appearance after quenching is identical with the conditions before quenching. However uncertain the quenching results may be, they clearly pose the question of whether, or when the agglomerates become fully liquid and whether or when impurities are retracted or boiled out of the aluminum interior.

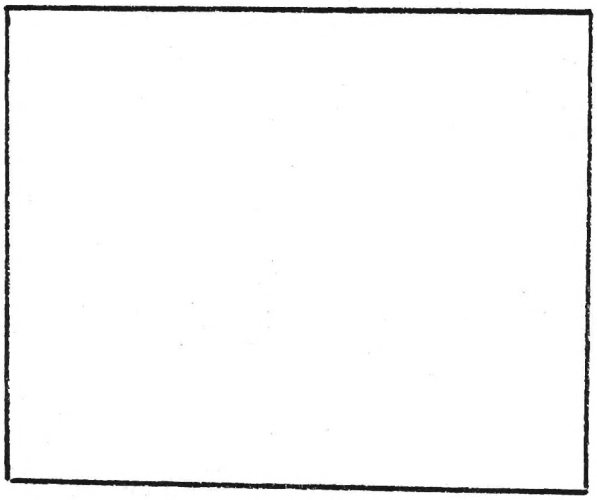
Given the qualitative nature of observations and the complexity of the transition from an accumulate to a fully burning droplet, and given the complex and uncertain combustion environment, it is not surprising that there are remaining uncertainties about the nature of agglomerates. However, the available evidence, in the form of real-time observations during actual combustion of propellants, indicatesthat the agglomerate eventually exhibits the combustion characteristics of aluminum droplets in oxygen-containing atmospheres. A molten aluminum droplet with an oxide lobe is visible whenever the flame sheath is not too bright to see through. Whether impurities in the Al and Al_2O_3 are large, or important to subsequent combustion is not known.

In summary, there is physical reason and observational evidence that the agglomerate involved in the early burning history of aluminum in motor situations is an object of considerable complexity, although it often exhibits superficial appearance of an aluminum droplet with retracted oxide lobe. It is not clear whether, or when the agglomerate actually approximates the physical structure of a burning aluminum droplet, although its combustion characteristics are similar.

7.4 Steady State Droplet Burning

During the time that the agglomerate is forming up and becoming fully inflamed, it also usually proceeds far enough from the propellant surface so that other combustion reactions (binder and oxidizer) are largely completed (e.g., 2500 μm from the surface). The gaseous environment is at a temperature of about 2300°C, and is composed primarily of H_2O, CO_2, CO, N_2, and HCl. The aluminum flame envelope is at a higher temperature due to exothermicity of the oxidation; burning of the droplet is governed by the flame envelope and may be erratic if the droplet is not above 2040°C, as the surface oxide is solid below this temperature. At the higher temperatures, the aluminum droplet then burns in the free volume of the combustor, forming primarily Al_2O_3 (ℓ) with corresponding decreases in the H_2O and CO_2, and increases in H_2 and CO.

The qualitative aspects of droplet burning are illustrated in Fig. 50. Aluminum evaporates and reacts to sub-oxides above the droplet surface, and eventually to Al_2O_3 droplets in a complex nucleation-heterogeneous reaction in which disposal of excess heat by radiation from oxide droplets is an important rate consideration (R-92) (the Al_2O_3 molecule dissociates when temperatures are high enough to give a vapor state, but will form at a net positive rate by heterogeneous reaction on an Al_2O_3 droplet provided the droplet temperature is below about 3800°C). The droplets in the flame sheath grow to 1 - 2 μm diameter due to the heterogeneous reaction, while new ones are nucleated to give a size population extending down to the limits of resolution. The appearance of a thin flame sheet implies that the oxide cloud is stagnant, i.e., there is no net production of gas inside the flame sheath (primarily because the aluminum goes to a condensed



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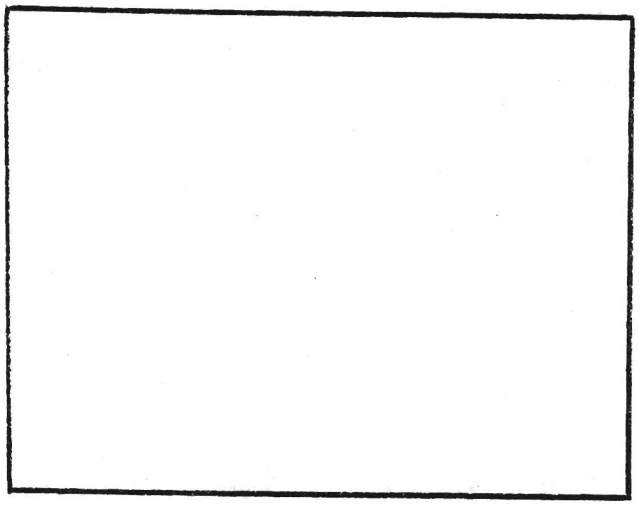

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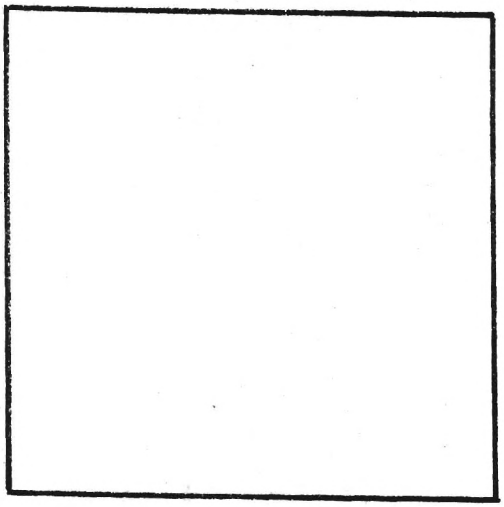


50 c

Fig. 50 Qualitative aspects of aluminum droplet burning: Part a, Sketch identifying regions of droplet and flame (left), and diffusion reactive species (right); Part b, Pictures of agglomerate burning immediately after leaving propellant surface, showing regions noted in Part a; Part c, Picture of agglomerate burning, using back lighting to show persistence of the smoke trails after leaving the droplet reaction region (lower luminosity reflects cooling from aluminum flame temperature to propellant flame temperature).

product). While this is implied by observations in both APCA tests and propellant combustion photography, it seems unlikely that it would be consistently true in all relevant gaseous environments at all pressures. In any case, the cloud is dispersed by convection associated with relative motion of the droplet in the environment in most situations (illustrated in Fig. 2, 50). In the rocket motor an aluminum droplet will usually experience convective flow, turbulence, and progressive depletion of oxidizing species during its burning history. These complexities are not contained in analytical models of combustion -- nor do existing experiments go far towards revealing their effects.

Looking further at the droplet combustion, it is observed in almost all experimental situations that there is appreciable oxide on the droplet burning surface. This may result from a variety of processes in propellant burning:

1. The agglomerate is made up of many ingredient particles, each of which had surface oxide.
2. Oxidation occurs to some degree during the sintering and ignition that produce the agglomerate.
3. In convective situations, oxide smoke may penetrate to the agglomerate surface.
4. Lower oxides of aluminum may diffuse to the agglomerate surface and "condense" to Al_2O_3 on the surface (R-93). It has been suggested that oxide accumulation is due to smoke diffusion given in quiescent atmosphere. However, the net gas flow is <u>outward</u> from the surface, and it is not clear that droplets would diffuse at an appreciable rate counter to the gas flow.

The relative role of these processes is no doubt dependent on the particular

situation, but has not been fully investigated. In APCA tests, oxide lobes develop during burning in free fall (R-94), suggesting that molecular diffusion and surface reaction are plausible.

Whatever the source of surface oxide, it becomes a dominant part of the burning agglomerate as burning progresses. Under most conditions the result is a "bilobate" droplet in which the dominance of the oxide modifies the burning characteristics (and violates assumptions of analytical models).

A matter of practical concern is the burning rate (or time) of agglomerates, this being of interest particularly in order to determine conditions that might give incomplete combustion in a motor. This information promises to be important also in determining the spatial distribution of burning droplets and product droplets, information needed to calculate the combustor stability to oscillatory disturbances. The general theory for diffusion-controlled combustion of hydrocarbon fuel droplets gives a burning time dependence on initial droplet diameter and pressure of the form

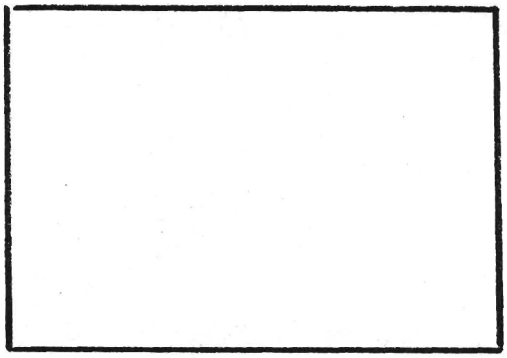
$$\tau \propto kD^n$$

with the value of n being 2, and k being a function of pressure and fuel-oxidizer properties and concentrations. A similar correlation has been argued for aluminum droplet burning (R-95), and is predicted by the theory of Ref. 96, but it appears that a value of n of 1.5 to 1.75 may be more appropriate (R-97), with the corresponding value of k being (for n = 1.5)

$$k = 6.7 \times 10^{-3} / \alpha_k^{0.9}$$

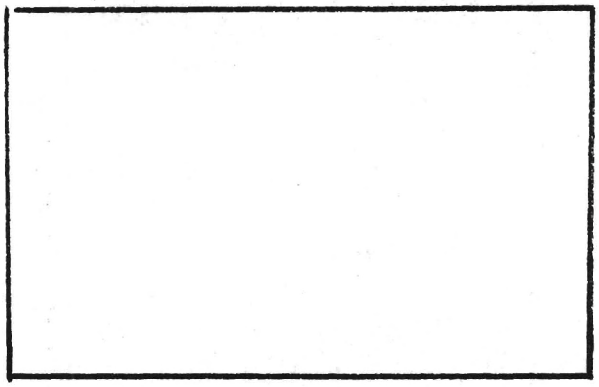
(τ in milliseconds and D in micrometers). In this expression α_k is the mole fraction of oxidizing species in the atmosphere and the number 6.7 (R-98) is a function of pressure, oxidizer properties and a weak function of atmospheric temperature. It should be stressed that the extent of initial surface oxide on an agglomerate, the portion of subsequent oxide accumulation and/or formation on the surface, the duration of the "steady state" phase of burning, and the nature of the behavior terminating (and following) the steady state phase are all known on speculative grounds only (because of uncertain relevance of APCA tests, and observational difficulties with motor-like conditions). Fig. 51 shows sample burning time data from various experiments.

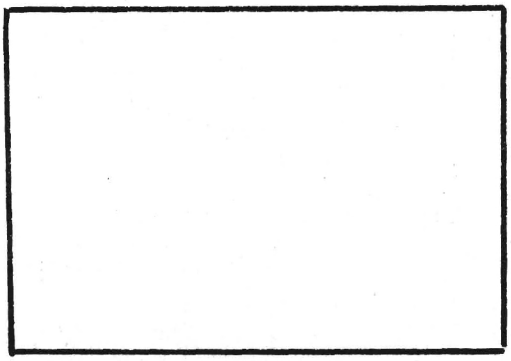
As a matter of completeness, some comment should be made on the progress of analytical modeling of aluminum droplet combustion as it relates to propellant combustion. Of the various models (R-99), that developed in Ref. 100 and extended in Ref. 101 seems most relevant to the present subject. For reasons of mathematical tractability, the models do not deal with the asymmetrical accumulation of oxide on the droplet



Part a, Measurements for μm droplets burning at one atm. in a atmosphere.

Part b, Measurements for μm droplets burning at atm. in gas burner flame products.





Part c, Measurements from propellant combustion at atm.

Fig. 51 Burning time of aluminum droplets.

surface, or with detailed chemical kinetics, droplet nucleation, etc. However, Ref. 100 does describe a model with detached flame and condensed reaction product, while Ref. 101 includes also heat release at the droplet surface due to formation of Al_2O_3. Other effects of the surface oxide are neglected.

Much of the insight into aluminum droplet combustion has come from efforts to reconcile various analytical models with experimental observations. As an example, one model (R-102) pictured the Al_2O_3 formation as occurring primarily on the droplet surface, forming a shell through which aluminum and oxidizing species diffused and reacted; however, such a model is incompatible with the observed droplet burning rate, the observed tendency to form an oxide lobe, and the observed smoke veil about the droplet. The model may have some relevance to the behavior in dilute atmospheres or towards the end of droplet burning when surface oxide dominates. The detached flame model in Ref. 100 was motivated by the experimental observation of a very hot, luminous detached flame envelope, and the addition of a surface heat release (R-101) was an effort to accomodate to the observation that surface oxide accumulated during burning. To date the analyses are of value primarily because they confront the mechanistic issues of the combustion precisely and suggest ways to test hypotheses and classify domains of behavior. A combination of experimental and analytical results also permits a basis for calculation of distribution of combustion in a motor, combustion efficiency, and an estimate of the response of the combustion cloud to flow disturbances. All such estimates are, of course,

limited by the uncertainty of the portion of burning in which the steady state model pertains, i.e., before the surface oxide dominates or droplet disruptions occur.

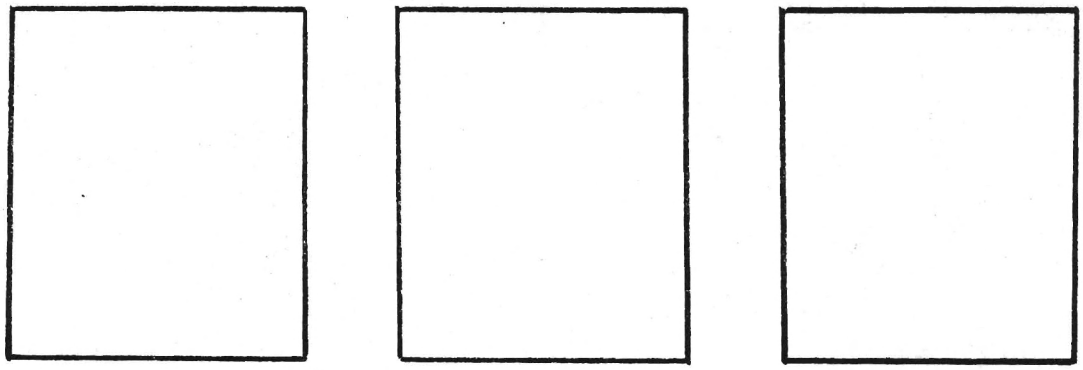
7.5 Terminal Phase of Droplet Burning and Products

The observation of spectacular fragmentations of aluminum droplets burning in air (Fig. 51-52) has led to considerable speculation about the mechanisms involved and their relation to motor behavior. The APCA tests (Section 7.2) have revealed that the terminal phase of burning can be both complex and varied. Interestingly enough, there is no evidence that fragmentation occurs in rocket motors, so the speculations could be purely academic excursions on the way to direct dismissal of the subject. In considering this possibility, one should keep in mind the following:

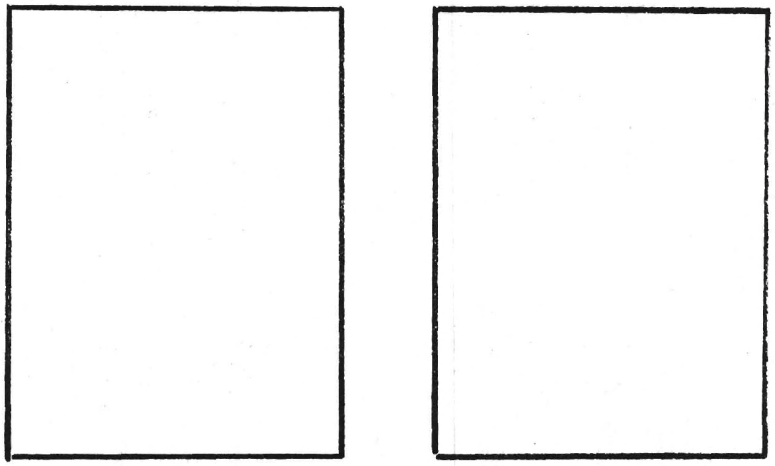
a. In the smoky environments fully representative of the rocket motor situation, observations do not show that fragmentations do not occur. Window bomb photography generally reveals no fragmentation, but does not simulate rocket motor conditions in the terminal phase of burning (indeed, most of the photography is designed to show the initial phase).

b. Accumulation of surface oxide on the burning droplets very likely does lead to some kind of transition in behavior towards the end of burning.

c. The aluminum oxide product droplet size is a matter of considerable practical concern, and the larger droplets are presumably formed from the surface oxide on the droplet. The droplet size distributions measured from samples of product oxide has not yet been rationalized on the basis of observed initial agglomerate



Part a, Successive frames of motion picture, showing fragmentation in a CO/O_2 gas burner experiment.



Part b, Track Photographs of droplet burning in ambient air, with sputtering and fragmentation.

Fig. 52 Fragmentation in the latter part of burning.

sizes and burning without fragmentation, although the subject is under investigation (R-103).

By the time an agglomerate has burned 70 or 80% of its aluminum, it has clearly formed a great deal of fine oxide smoke. This conclusion is supported by all experiments. It is less clear how much surface oxide exists, or what portion of it was present at the time of agglomeration (R-104). The amounts are definitely affected by events prior to full inflammation, and by the nature of the gaseous atmosphere (e.g., in APCA tests). The evidence in rocket motor-like environments suggests that 5 - 30% of the aluminum ends up in oxide droplets far too large to be the product of the detached flame (sizes above 4 μm are probably not formed in the flame), and some of this oxide is clearly visible in combustion photography of agglomerates early in burning (Fig. 2, 32) and on samples quenched later in burning (R-105).

As the amount of aluminum in the burning agglomerate decreases, the accumulation of oxide becomes an increasingly important factor in the droplet burning, and APCA tests show that oxide may envelop the droplet, or be partially ejected, or participate in violent fragmentation of the droplet. Such events affect both the subsequent combustion rate and the size distribution of oxide droplets formed from the surface oxide. It is not known to what extent the surface oxide becomes subdivided in rocket motor combustion, because of observational difficulties. However, the issue is not trivial because the oxide droplet size distribution is important to combustor stability, nozzle erosion, nozzle efficiency, and exhaust plume effects. The view of the general propulsion community is that the oxide is mostly less than 2 micrometer, a view stimulated by the high visibility of the larger weight fraction (smoke oxide) that is in that size range.

This view is reinforced by extensive measurements in the exhaust plume, measurements that are probably biased by poor sampling-measurement methods, and which reflect also changes in size distribution in the nozzle flow. A few quick calculations establish reasonable perspective on the question of size distribution and the measurement problem.

Consider the following relationships among ingredient particle size, agglomerate size, and oxide droplet size:

Relation between Ingredient Particle Diameter and Agglomerate Diameter	$n_{Al} D_{Al}^3 = D_{aggl}^3$
Diameter of Residual Oxide Droplet	$D_{oxr} = D_{aggl} \left(\frac{102}{54} \frac{K}{100} \frac{n_{aggl}}{n_{ox}} \frac{\rho_{Al}}{\rho_{ox}} \right)^{1/3}$
Number of Oxide Droplets from an Aluminum Droplet	$n_{ox} = \frac{102}{54} \frac{K}{100} \frac{\rho_{Al}}{\rho_{ox}} n_{aggl} \left(\frac{D_{aggl}}{D_{ox}} \right)^3$

In these relations, K is the percent of oxide in the form in question, and 102/54 is the molecular weight of Al_2O_3 relative to the constituent aluminum. Using these relations, consider the following example: $D_{Al} = 15$ μm, $D_{aggl} = 100$ μm, $D_{oxs} = 1$ μ, and K = 20% for residual oxide, 80% for smoke. From the above equations taken in sequence:

a) There are 296 ingredient particles per agglomerate

b) The residual oxide droplet is 64 μm in diameter (if all the surface oxide goes to one residual)

c) The smoke droplets would number about 10^6.

d) The number of particles per gram of propellant is enormous. For a propellant with 15% aluminum,

Ingredient particles, $n_{Al} \simeq 3 \times 10^7$

100 μm agglomerates, $n_{aggl} \simeq 10^5$

64 μm residual oxides, $n_{ox\ r} \simeq 10^5$

1 μm smoke droplets, $n_{ox\ s} \simeq 10^{11}$

From this sample calculation it is easy to see why the residual oxide droplets could be missed in experiments and size distribution measurements, although their presence is unambiguous when care is taken in sample collection and separation by size (R-106; Fig. 53). It is worth restating that the 20% of residual oxide is often important in propellant and motor designs, especially relative to combustor stability in the less-than-1000-hz range, and relative to two-phase flow effects in the nozzle. It's even important to calculations of size distribution changes in the combustor and nozzle flow, where the initial combustion-generated bimodal nature of the droplet distribution has generally been ignored in published work (R-107).

So where do we stand on the question of oxide droplet size distribution? As far as the size distribution produced by the propellant combustion, there is no doubt that there are two size ranges involved (smoke, <2 μm, and "residuals", 2 - 100 μm : Fig. 3). These are produced by different paths in combustion of the agglomerates. The smoke droplets constitute 70% or more of the mass of oxide (R-108). The size of the residuals is dependent on the size of the aluminum droplets and factors governing that size, such as propellant variables, pressure and flow environment. Determinations of oxide droplet size distribution are very difficult, at 3 different levels: a) conducting an experiment that simulates a rocket motor environment; b) collecting and sampling the product oxide in a way that doesn't bias the size distribution; and c) measuring a size distribution from <0.1 μm to 1000 μm without biasing the results. On the fundamental side, it remains

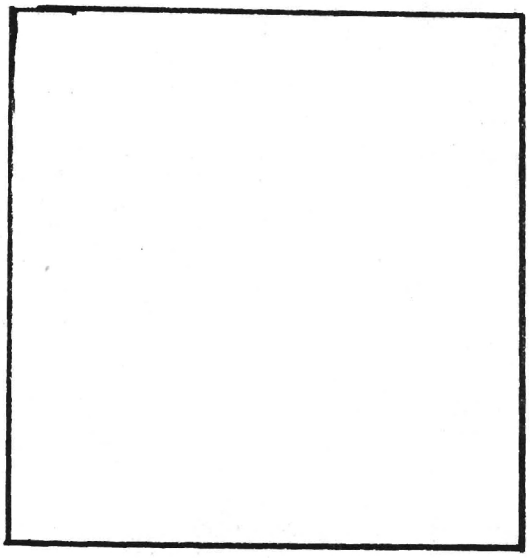


Fig. 53 Photomicrograph of a size fraction of residual oxide droplets, separated from a sample of oxide products of a propellant burning in a closed system.

uncertain how much residual oxide is present in the products, how much of it is formed prior to separation of the aluminum from the propellant burning surface, whether or not the accumulating oxide in the agglomerate is usually subdivided by fragmentation or other process, or how great the effects of combustor flow (acting through size-limiting of agglomerates) are on oxide size. That some of these issues are non-trivial is indicated by Reference 109 and Fig. 54. The figure shows the effect of flow environment on size distribution of collected oxide in tests in a closed system where most of the oxide > 4 microns is collected. Later tests using a more limited range of flow conditions but more refined sample collection-measurement technique (R-110) indicate the same flow effects, which are also inevitably present in rocket motors.

7.6 Summary of "Combustion and Products"

This aspect of the aluminum behavior is perhaps both the most studied and least understood of those discussed. The APCA tests demonstrate many combustion phenomena, but don't tell which are relevant to propellant combustion. The analytical models explain certain aspects of observed behavior, but fail to accomodate the formation and/or presence of retracted surface oxide, which is observed in both APCA and propellant tests. Neither APCA tests or analytical models approximate the high pressure, high temperature, complex chemistry or convective nature of the motor environment or the physical and chemical complexity of the aluminum agglomerate. Efforts to obtain information directly from propellant combustion are hampered by the usual difficulties of high pressure, high temperature, high speed, microscopic processes, complicated further by the ever-present obscuration of observation by dense Al_2O_3 smoke. Even observation of the oxide reaction products is

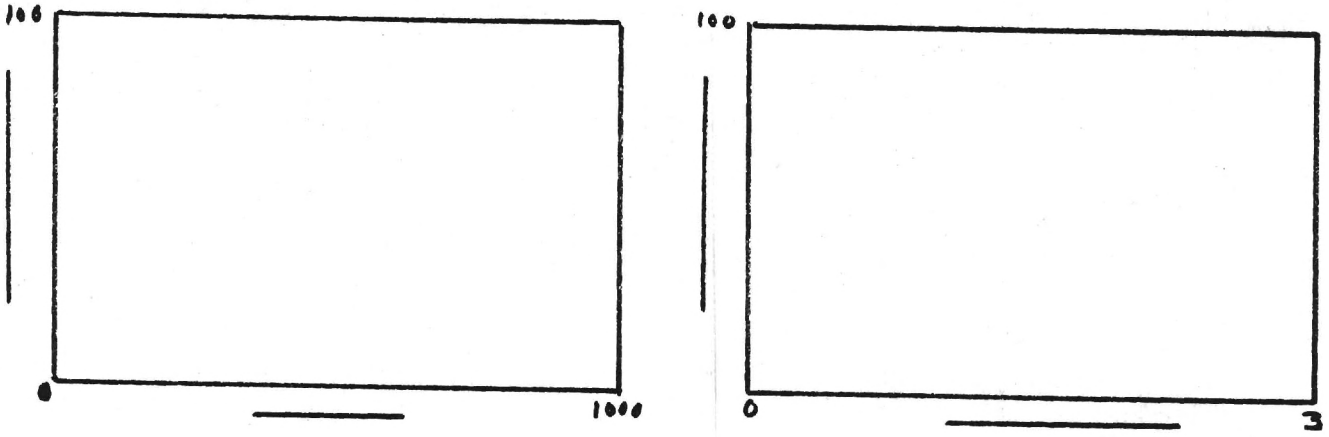


Fig. 54 Effect of combustor flow on residual oxide size distribution. In a 2-in. diameter burner, tests were run on end-burner propellant samples and on tubular samples of 3 different lengths. The graphs show the change in oxide mass fraction in 3 particle size intervals, vs sample length (with end burners at zero length). Increasing flow (sample length) reduces the coarse mass fraction, increases the fine.

difficult, hampered by the difficulty of unbiased and quantitative collection and measurement in a medium with such a wide particle size range and vast numbers of particles.

There is no doubt that agglomerates burn with an oxide lobe and a detached flame with smoke veil (although it is not known what portion of the surface oxide is formed before and during ignition, what portion during burning). There is no doubt that the majority of the oxide is formed in the flame (smoke), although the surface (residual) oxide is important. It is not known whether the latter part of the agglomerate burning history has any of the singular events like fragmentation seen in some APCA tests. However, it is clear that the oxide products have a bimodal size distribution corresponding to smoke and surface oxide. There is some uncertainty as to how closely agglomerate behavior corresponds to pure aluminum droplet behavior. Agglomerate burning times are known approximately, and it is clear that an appreciable portion of the combustor volume is occupied by burning droplets; in some cases combustion is incomplete at the nozzle entrance.

DISCUSSION

8.1 Rationale of This Report

This report has sought to bring together the many observations and mechanistic arguments that constitute our present understanding of how the aluminum powder ingredient in solid propellants behaves during combustion. The seemingly ponderous detail involved reflects a complexity of the overall process, in which the outcome of the overall process is strongly dependent on the detailed steps. This dependence arises from the many factors that affect agglomerate formation, and the large effect that agglomerate size has on combustion and nozzle efficiency, combustion stability, nozzle erosion, and exhaust plume effects. The approach in this report has been to describe the process up to completion of combustion and characterization of oxide products, with only passing reference to the application to specific motor environments. There are limits to what can be done in one report. The overall combustion process is outlined in Fig. 15, and involves concentration of aluminum on the burning surface, followed by coalescence, ignition and departure from the surface as relatively large burning "agglomerate" droplets. These droplets burn as they move out in the product flow, forming a bimodal population of oxide droplets. This two phase medium plays an important role in combustion stability, nozzle efficiency, erosion, etc.

8.2 Outstanding Fundamental Questions

There are a number of very detailed questions about aluminum behavior that are important to motor performance but remain unanswered to date, and the best service to the reader may be a summary of such unanswered questions. Most are important to mechanistic arguments, which in turn contribute to

rational and innovative attack on practical problems. Typical areas of controversy or ignorance are:

1. There is still not much known about the oxide skin on ingredient aluminum particles, and no quality control specifications are used. However the oxide skin is an important factor in agglomeration.
2. A scheme, called the "pocket model" was contrived many years ago to describe how the size of agglomerates is determined. While this model depends heavily on the microstructure of propellants with narrow oxidizer particle size distribution, it is both used and criticized in other situations. This behavior reflects a need and failure to find a more complete scheme for describing agglomeration.
3. The binder plays an important role in retention and concentration of aluminum on the burning surface, but the substantial differences due to contrasting behavior of different binders are only superficially known.
4. The reluctance of aluminum to ignite in the presence of pyrolizing binder or oxidizer accounts for the opportunity for concentration in the burning surface. The encroachment of diffusion flamelets seems to be critical to ignition of the accumulating aluminum. However we know very little about the diffusion flame behavior, even in the absence of aluminum. Further, the aluminum ignition process itself has not been studied under motor-like conditions.
5. Combustion of agglomerates may start on the propellant surface or after departure. In some cases of ignition on the surface, burning persists on the surface. These "habits" are discussed in the text and are partly understood in terms of type of binder,

proximity of diffusion flame, etc. However it is difficult to understand how fully burning agglomerates of only moderate size can linger stationary on the burning surface, as sometimes occurs even under favorable burning conditions.

6. The transition from sintered accumulates of aluminum particles to a single spherical agglomerate is an exceedingly complex event. It is not clear when the agglomerate becomes a simple burning droplet with oxide lobes, but there remains considerable controversy as to the condition of those objects seen in combustion photography as fully formed droplets. Quench tests near the burning surface give complex objects. This raises some doubt as to the validity of droplet size measurements made from movies. Chemical impurity also raises questions about subsequent combustion details.
7. Aluminum oxidation no doubt occurs while the aluminum sinters on the burning surface. This accounts for some of the surface oxide that leads to the larger "residual" oxide droplets in the reaction products. However the extent of this oxidation and other contributions to the residual oxide droplets remains undetermined.
8. There is some controversy as to whether surface oxidation occurs on the burning agglomerate (oxide definitely accumulates on the surface in O_2/N_2 atmospheres, but there is disagreement about how it gets there: See Section 7).
9. Valid determination of burning time in motor-like environments has not been made, particularly because the oxide smoke obstructs the view. While estimates can be made, the quantitative data needed to evaluate analytical models is lacking.
10. Analytical modeling ignores the effect of oxide lobes on the droplets,

which probably affect droplet burning appreciably even before they induce the various anomalies near burnout. The burning time laws such as

$$\tau = kp^n$$

cannot be expected to describe correctly the burning of two 100 μm droplets, one of which just ignited and another of which has burned down from 200 μm (at 100 μm they have very different oxide lobes).

11. Because of the obscuration by smoke, the details of the terminal phase of burning are unknown. Specifically, it is not known whether fragmentation or subdivision of the surface oxide occurs, or under what conditions.

12. It is expected that the responsiveness of surface accumulation-agglomeration-shedding of aluminum to imposed flow environments is important to the overall combustion behavior and two-phase media flow effects. To date the study of these effects is limited.

13. The description in this report pertains particularly to propellants having ammonium perchlorate oxidizer, propellants for which large amounts of unclassified information is available. Futher systematic studies with propellants containing nitramines, energetic plasticizers, and burning rate modifiers are needed before many generalizations regarding them can be made. In general, burning rate catalysts appear to bring the diffusion flamelets in closer, promoting ignition and reducing agglomeration size. Other changes tend to aid aluminum ignition if they raise the flame temperature, hinder ignition if they lower the oxidizing potential of the combustion zone.

8.3 The Practical Problems and Research

A candid observer may reasonably ask, who cares about all these details regarding combustion of aluminum? Aren't the rocket motors actually performing all right? Can any great economy or performance benefit be gained by knowing more? If more must be learned, what is most important? These questions were anticipated in the Introduction (Section 1), and are partially answered there. The benefits and penalties of aluminum fuel listed there have all been realized in one application or another. But now, with a more complete understanding of how aluminum behaves, perhaps a more penetrating look at applications of knowledge is possible.

Do we have to exert great care in order to realize the improvement in propellant performance promised by the "equilibrium" thermochemical performance calculations? In large motors with high operating pressure, the answer is "no". Combustion efficiency is high because stay-time of droplets in large motors is long, the droplet burning rates are high at the high pressures used, and the agglomerate droplets are small due to the high pressure and catalyzed propellants used. Further, the nozzle losses due to 2-phase flow are low because the droplet lag is small in large nozzles.

On the other extreme, conditions in upper stage and space motors (where combustion efficiency is critical) tend to be the opposite; large agglomerates, low droplet burning rates, and short stay times, all conducive to low combustion efficiency. In addition, the large oxide droplets, low gas density, limited nozzle size and use of complex geometry (e.g., submerged nozzles) all contribute to low nozzle efficiency in such motors. These problems with aluminum as a fuel are more prevalent than is generally acknowledged, although most propulsion engineers will agree that the aluminum content

in the propellant is kept well below the theoretical optimum because of poor performance at high aluminum content.

Perhaps of greatest practical importance to the propulsion engineer is not the loss in efficiency, but rather the realization that conditions conducive to low combustion efficiency are also conditions where variability of performance is probable, where combustion is marginally stable, where ignition is difficult, where exhaust plumes contain burning aluminum, and where marginality of most functioning imposes increased demands on quality control product-surveillance for constancy with aging. Certainly any detailed knowledge about aluminum behavior that permits beneficial modification in propellants or design, or better choice of ingredient control to reduce the marginality of combustion merits serious consideration.

Combustion efficiency is acknowledged to be a problem only under extreme conditions such as low pressure, but combustor instability is a widely recognized problem, which can occur under routine conditions, governed by no simple rules. Combustion instability (oscillatory combustion) has been the motivation for much of the research on aluminum combustion. Present understanding offers some interesting possibilities for anticipating, avoiding, or remedying combustion instability. It is easy to argue that the foreseeable benefits of the research will never pay for the cost of research, and propulsion engineers usually find a way out of instability problems by some insight and trial and error. The reality is that the combined cost of combustion instability problems in development programs is of the order 10 to 100 times greater than expenditures for related combustion research, with these costs contributing little or nothing to subsequent programs where the problem recurs. By comparison, the mechanistic understanding, ballistic tests,

analytical models and computer programs produced by research programs are having a growing impact on propellant and motor design, with a corresponding reduction of risk of combustion instability.

Some of the emerging understanding of aluminum combustion is relevant to emerging problems such as exhaust plume visibility, contamination of launchers and spacecraft, and stratospheric pollution. The extent to which understanding of combustion can help resolve these and other problems remains to be seen. In the meantime it is important that the available knowledge be applied to the practical problems to which it is clearly applicable.

APPENDIX A

Definition of Terms

Accumulate - noun - accumulated material that has become stuck together into an identifiable increment of such material.

Accumulation - concentration of some ingredient (usually of aluminum) or product on the burning surface due to lingering there while the surface recedes.

Adhesion - sticking together of material elements to each other by virtue of an intermediate agent (e.g., aluminum particles stuck together by melted binder).

Agglomerate - noun - an assemblage of aluminum particles that has coalesced; such coalescence usually follows breakdown of the protective oxide skin, and is accompanied by ignition unless some quenching process occurs.

Coalescence - the merging together of two or more particles to such an extent that the identity of the original particles is lost.

Cohesion - sticking together of two or more particles by their own interaction (e.g., oxide-coated aluminum particles stuck together by building of an oxide or metal bridge joining particles).

Filigree - an accumulate of low "packing density", exhibiting a "lacy" structure. In combustion photography, filigrees often appear to be only tenuously attached to the burning surface.

Ignition - onset of self-sustaining combustion. In the case of aluminum this is usually accompanied by appearance of an Al_2O_3 smoke trail, and by coalescence of one or more accumulates into an agglomerate.

Inflamation - propagation of an ignited condition from its point of origin, into a connected accumulate structure, usually leading to formation of one or more agglomerates.

Sintering - used in a special sense here to describe oxidative welding of oxide coated aluminum particles to each other, like the example of "cohesion" described above.

Abbreviations

Al -	aluminum
AP -	ammonium perchlorate
DB -	double base, referring to propellants made from nitrocellulose and a second active (gelling) ingredient such as nitroglycerin or dinitrotoluene
DSC -	differential scanning calorimeter
DTA -	differential thermal analysis
HC binder -	hydrocarbon (synthetic rubber) binder
HPD -	hot plate drop test
HSM -	hot stage microscope
NC -	nitrocellulose
NG -	nitroglycerin
SEM -	scanning electron microscope

POLICY ON REFERENCES

Text References and the Bibiliography

The procedure in making text references to other literature consisted of insertion of "R" numbers, e.g., R-57 in the text. Any one "R" number refers to one or more of the numbered entries in the Alphabetical Bibliography. The connection between the "R" number and the Bibliography numbers is given in the Reference-Bibliography Number Code. This procedure was used for convenience, particularly in view of the probability that additional entries will be made by NWC into the Bibliography. The procedure is also advantageous when certain bibliographical entries are used frequently. It will be noted that "R" numbers are introduced serially in the text. However, in one or two cases, (like R-7 and R-11), an "R" number has more than one part (e.g., R-7a, R-7b, R-7c), and in two instances "R" numbers are skipped -- i.e.,not used (R-33 and R-96). In the Alphabetical Bibliography, one Reference number (208) was not used. These anomalies arose from oversight and should be corrected by re-numbering in the text and the Number Code prior to final typing (this correction was made several times previously, but recurred due to revisions in the text). Since NWC will no doubt want to make further changes before final typing, it was judged unimportant to correct the numbering anomalies so long as they did not represent ambiguities (re-numbering will be necessary for any NWC changes anyway).

The Bibliography

Because of the large number of references and repeated use of many of them, it was judged inappropriate to put references at the bottom of the pages (e.g. R-4 represents 36 references). Further, it was judged appropriate to include many relevant bibliographical entries that were not explicitly cited in the text (i.e., in the Reference-Bibliography Number Code). For these reasons it was judged preferable to use an alphabetized bibliography, which is included. However the original bibliography was updated to accomodate revisions of the text and review of initially unavailable literature. This up-dating was done by simply adding an alphabetized Supplementary Bibliography. Correlation of these entries with the relevant R numbers was accomplished by addition of entries with the prefix S into the Number Code. After further NWC additions, made in a similar way, the whole Bibliography should be consolidated alphabetically, re-numbered, and the Number Code entries modified correspondingly. No attempt was made to complete this consolidation because the result would have to be redone after NWC changes.

Choice of References

In general, references (i.e. bibliographical entries) were chosen for relevance to the content of the text. Several points merit further attention.

1. Some bibliographical entries may refer to early versions of research work later published in more final form. Time and resources did not permit complete remedy of this problem, and NWC reviewers may wish to make appropriate substitutions.
2. The most recent publications were not consistently available. For example, some recent, relevant NWC reports were not received or went astray (e.g., NWC TP 5569). Since the list will never be completely up to date for long, this may not merit further effort.
3. In both text content and references, reliance on NWC work is very heavy, as the program of study there has been relatively thorough. Further, it was intended that the report serve as a summary of NWC work as well as a broader survey. It is particularly appropriate that NWC reviewers add relevant references, correct errors of authorship, etc. (some NWC reports did not list authors explicitly but writing was organized or dominated by some one member of the team, or by a project leader).
4. Many of the references were originally published with "limited distribution statements". It was considered to be impractical to avoid such references. However classified references were largely avoided (some references were originally classified and

later declassified). References that are still classified are so marked, and the text presents no specific information from such references that is not revealed by the unclassified titles.

5. The source of bibliographical entries is often identified by the initials of the originating agency. In the interest of compactness, such abbreviations were retained. For completeness, a Glossary of such abbreviations is included with the Bibliography.

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GLOSSARY OF ABBREVIATIONS

AFRPL - (U. S.) Air Force Rocket Propulsion Laboratory, Edwards, California

AGARD - The Advisory Group for Aerospace Research and Development of NATO (North Atlantic Treaty Organization)

AIAA - American Institute of Aeronautics and Astronautics, New York City

ARS - American Rocket Society (a predecessor of AIAA)

ATD - Aerospace Technology Division, Library of Congress

CI - The Combustion Institute, Pittsburgh, Pennsylvania

CPIA - Chemical Propulsion Information Agency, Johns Hopkins University, Applied Physics Laboratory, Laurel, Maryland

ERDE - Explosives Research and Defense Establishment, England

IAS - Institute of Aeronautical Sciences; Institute of Aerospace Sciences (a predecessor of AIAA)

ICRPG - Interagency Chemical Rocket Propulsion Group (predecessor of JANNAF)

JANNAF - Joint Army Navy NASA Air Force Working Group on Combustion

NACA - National Advisory Committee for Aeronautics, Washington, D.C. (predecessor of NASA)

NASA - National Aeronautics and Space Administration, Washington, D.C.

NATO - North Atlantic Treaty Organization, Paris

NOTS - (U. S.) Naval Ordnance Test Station, China Lake, California

NWC - (U. S.) Naval Weapons Center, China Lake, California

ODDRE - Office of the Director of Defense Research and Engineering, U. S. Department of Defense, Washington, D.C.

ONERA - Office Nationale d'Etudes et de Recherches Aerospatiales, Chatillon, France

RPE - Rocket Propulsion Establishment, England

SNPE - Societe Nationale des Poudres et Explosifs, Paris

UARL - United Aircraft Corporation Research Laboratories, East Hartford, Connecticut

UTC - United Technology Center; now Chemical Systems Division, United Technologies, Sunnyvale, California

WSS-CI - Western States Section, The Combustion Institute

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